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REMOVAL OF COLOR, DETERGENTS, AND OTHER REFRACTORY SUBSTANCES FROM TEXTILE WASTEWATER

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16. ABSTRACT

The report gives results of laboratory and pilot scale research to determine the effectiveness and economic feasibility of various physicochemical tertiary treatments in removing color, detergents, and other refractory pollutants from textile wastewater that has been previously treated biologically with activated sludge. Tertiary treatments included filtration on single and dual media filters, conventional and contact coagulation, adsorption on granular activated carbon, oxidation with ozone, ion exchange on anionic and cationic resins, and hyperfiltration. Each treatment was investigated individually and in combined systems. Results indicate that all tertiary treatments were effective in removing individual pollutants. However, feasibility of the processes (determined by economic factors, energy consumption, and technical availability) differed considerably. Hyperfiltration is more energy intensive than the other tertiary treatments. Ion-exchange resulted in poor COD removal and a large amount of post-generation wastewater. The most effective combined tertiary treatment consisted of contact coagulation on upflow filters, followed by dual media filtrations. The filtrations were preceded by chlorination with NaOCl and followed by adsorption on activated carbon as the final step.

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ABSTRACT

The following report, covering the period from June 30, 1972 to June 29, 1977, was submitted in fulfillment of Contract No. PR-5-532-3 by the Water Renovation Section, Institute of Meteorology and Water Management, Cracow Division, under the sponsorship of the U.S. Environmental Protection Agency.

The laboratory and pilot scale research was carried out in order to determine the effectiveness and economic feasibility of selected, advanced physicochemical treatment processes for the removal of color, detergents, and other refractory pollutants from wastewater. The subject of the research was mixed textile and municipal wastewater that had previously been biologically treated by means of activated sludge. The advanced tertiary processes studies included:

- Filtration on single and dual media filters (anthracite and sand),
- conventional and contact coagulation,
- adsorption on granular activated carbon,
- oxidation with ozone,
- ion exchange on anionic and cationic resins, and
- hyperfiltration (reverse osmosis) on spiral ROGA membrane.

All the processes were investigated both individually and in combined systems. Each process was initially tested on a laboratory scale and finally examined on a pilot scale at the experimental plant situated at the municipal wastewater treatment plant in Andrychow. The total amount of the raw wastewater according to the last assessment in 1976 was on the average 12,000 m^3/d. The proportion of textile to municipal wastewater was maintained within the range of 1:1 to 2:1. The research showed that all the processes studied succeed to a considerable degree in the removal of individual pollutants, although the feasibility of the processes as determined by economic factors, energy consumption, and technical availability differs.

The filtration of biologically treated wastewater reduces the concentration of suspended solids to below 10 mg/l, which represents a 30 to 75 percent removal of the wastewater BOD. Contaminants like COD, color, and detergents, that are characteristic of textile wastewater, are eliminated only to a small degree. Aluminum salts with oxidant and acid added for pH control should be used for coagulation. Contact coagulation in an upstream filter appears to be a better method than conventional coagulation.

The detailed investigation of the adsorption process has proved that the color substances present in biologically treated wastewater determine the proper kind of carbon, while the COD load determines the adsorption

capacity of the carbon. The removal of particular pollutants expressed in percentage is more complete for biologically treated and coagulated wastewater than for effluent treated only biologically.

The greatest energy consumption takes place in the hyperfiltration process as a result of very high wastewater pumping head. The energy consumption in ozone oxidation is also considerable, but this process is less effective than adsorption in the removal of COD. The ion-exchange process revealed considerable disadvantages: in particular, poor removal of COD and a large amount of post-regeneration wastewater.

In the last period of research, a combined system was investigated. Contact coagulation on upflow filters and dual media filtration preceded by chlorination with NaOCl and followed by adsorption on activated carbon as a final process was found to be the most effective of the combined technological processes.

CONTENTS

Page

Abstract iii
Figures vi
Tables xvi
Abbreviations and Symbols xxvi
Acknowledgments xxvii

1. Introduction 1
2. Conclusions 3
3. Recommendations 6
4. Procedure and Analytical Research 7
5. Characteristics of Textile Processes and Pilot Plant Operation 40
6. Filtration Process 62
7. Coagulation 119
8. Adsorption 179
9. Oxidation by Ozone 248
10. Ion Exchange 315
11. Hyperfiltration Process 415
12. Combined System and Comparison of Processes 431

References 437

Appendixes

A. Analytical Procedure for Selected Constituents 443
B. Method of Determining FINAD Index 445
C. Decree of the Ministry Council (Extract) 450

Glossary 455

FIGURES

Number Page

Section 4

4-1 Dependence between the reduction of the extinction and the wastewater dilution for various wavelengths 20

4-2 Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for Helasol Yellow GOK dye in water solution before and after isolation of dye on XAD-4 resin bed 21

4-3 Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for Helasol Yellow GOK dye in biologically treated wastewater before and after isolation of dye on XAD-4 resin bed 22

4-4 Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for wastewater of a characteristic blue-green color before and after isolation of color on XAD-4 resin bed 23

4-5 Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for wastewater of a natural yellow-green color concentrated before and after isolation of color on XAD-4 resin bed 24

4-6 Change of transmission spectrum in the λ value ranged blue 420 nm to 650 nm for wastewater of a characteristic blue-green color concentrated before and after isolation of color on XAD-4 resin bed 25

4-7 Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater on XAD-4 resin bed 26

4-8 Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater on XAD-4 resin bed 27

4-9 Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater by extraction 28

Number Page

Section 5

5-1 Finishing plant A. Schematic plan of the bleach and dye houses 44

5-2 Finishing plant B. Schematic plan of the bleach and dye houses 45

5-3 Finishing plant A. PAD-STEAM dyeing machine processes 46

5-4 Finishing plant B. PAD-STEAM dyeing machine processes 47

5-5 Finishing plant A. Bleach house 48

5-6 Finishing plant B. Bleach house 49

5-7 Schematic plan of the primary treatment plant and the pilot plant in Andrychow 51

5-8 Schematic diagram of the pilot plant filtration and adsorption installation 52

5-9 Schematic diagram of the pilot coagulation installation 53

5-10 Schematic diagram of the pilot upflow filtration installation 53

5-11 Schematic diagram of the pilot ion-exchange installation 53

5-12 Schematic diagram of the pilot ozone oxidation installation 53

5-13 Schematic diagram of the pilot installation for combined treatment processes 54

5-14 Hyperfiltration pilot plant diagram 55

5-15 Pilot plant time-phase diagram 56

Section 6

6-1 Experimental laboratory model for rapid filtration of secondary effluent 77

6-2 Efficiency of contaminant removal from biologically treated wastewater during the rapid filtration 78

Number Page

6-3 Pressure versus depth in a gravity filter at various times during a filter run. Single medium filter. First stage of investigations, laboratory scale 79

6-4 Pressure versus depth in a gravity filter at various times during a filter run. Dual media filter. First stage of investigations, laboratory scale 80

6-5 Scheme of apparatus applied for pilot plant wastewater filtration process 81

6-6 Screening curve of dual media filtration. Grain size distribution of a dual media filtration bed, columns B and C, pilot scale 82

6-7 Statistical variations in suspended solids during series I, pilot plant 83

6-8 Statistical variations in BOD during series I, pilot plant 84

6-9 Statistical variations in suspended solids during series II, pilot plant 85

6-10 Statistical variations in BOD during series II, pilot plant 86

6-11 Statistical variations in suspended solids during series III, pilot plant 87

6-12 Statistical variations in BOD during series III, pilot plant 88

6-13 Pressure versus depth in a gravity filter at various times during a filter run. Second stage of investigation, pilot plant 89

6-14 Variability of suspended solids content, during the time of the filtration cycle, in the influent and effluent from individual columns 90

6-15 Suspended solids concentration in wastewater at various depths of the filtration bed during the filter run, pilot plant, series IV 91

6-16 Variability of suspended solids content during the time of the filtration cycle in the influent and effluent, series V, second stage of investigation 92

Number Page

6-17 Suspended solids concentration in wastewater at various depths of the filtration bed during the filter run, pilot plant, series V 92

6-18 Course of the colored wastewater wave flow through particular layers of the bed during the filtration process, stage II, series V, measurement 1 93

6-19 Course of the colored wastewater wave flow through particular layers of the bed during the filtration process, stage II, series V, measurement 2 94

Section 7

7-1 The relative value of color removal according to coagulation time 139

7-2 Relation between color removal and coagulant dose for three pH values of wastewater 140

7-3 Relation between color removal and coagulant dose for three pH values of wastewater 141

7-4 Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 8 mg Cl_2/l NaOCl 142

7-5 Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 8 mg Cl_2/l NaOCl 143

7-6 Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 16 mg Cl_2/l NaOCl 144

7-7 Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 16 mg Cl_2/l NaOCl 145

7-8 Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 24 mg Cl_2/l NaOCl 146

7-9 Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 24 mg Cl_2/l NaOCl 147

7-10 Relation between color removal and dose of NaOCl for three pH values of wastewater 148

Number Page

7-11 Relation between color removal and coagulant dose of NaOCl for three pH values of wastewater 149

7-12 Average color removal in relation to the coagulant dose and pH value 150

7-13 Average color removal during the preliminary oxidation with NaOCl in relation to pH values 151

7-14 Relation between COD removal and coagulant dose for three pH values in wastewater 152

7-15 Relation between COD removal and coagulant dose for three pH values in wastewater 153

7-16 Relation between COD removal and coagulant dose for three pH values in wastewater 154

7-17 Relation between COD removal and coagulant dose for three pH values in wastewater 155

7-18 Average COD removal in relation to coagulant and pH values 155

7-19 Influence of preliminary oxidation before coagulation on COD removal 156

7-20 Relation between the nonionic detergent removal and coagulant dose for three pH values in wastewater 157

7-21 Relation between the nonionic detergent removal and coagulant dose for three pH values in wastewater 158

7-22 Average removal of nonionic detergents in relation to the coagulant dose and the pH values in wastewater 159

7-23 Influence of preliminary oxidation on nonionic detergent removal in wastewater after coagulation 160

7-24 Influence of oxidation with NaOCl on removal of residual aluminum from coagulated wastewater 161

7-25 Relation between the removal of color measured spectrophotometrically at λ = 400 nm and the dose of NaOCl added before coagulation with 200 mg $Al_2/SO_4/_3 \cdot 18H_2O/1$ 162

7-26 Relation between the removal of color measured spectrophotometrically at λ = 550 nm and the dose of NaOCl added before coagulation with 200 mg $Al_2/SO_4/_3 \cdot 18H_2O/1$ 163

Number Page

7-27 Upward flow filtration column used for contact coagulation 164

7-28 Coagulation reactor with suspended flocs 165

7-29 Flow time spectrum in filtration columns 166

Section 8

8-1 Determination of phenol number by the FINAD method 204

8-2 Determination of indole number by the FINAD method 204

8-3 Determination of detergent number by the FINAD method 205

8-4 Adsorptive capacity of activated carbons expressed by the FINAD indexes 206

8-5 Influence of contact time on change of COD, detergent, and color concentration in wastewater treated with Z-4 and Calgon 207

8-6 Influence of Z-4 dose on percent removal of COD and detergents (contact time = 0.5 h, pH = 7.8, room temperature) 208

8-7 Influence of Z-4 and Calgon dose on percent removal of COD, detergents, and color 209

8-8 Influence of Z-4, Calgon, and Hydrodarco dose on percent removal of detergents and color (contact time = 1 h, ph = 8.5, room temperature) 210

8-9 Adsorption isotherms for COD (contact time = 1 h, pH = 8.5, wastewater after biological treatment, room temperature) 211

8-10 Adsorption isotherms for COD (contact time = 1 h, pH = 7.7, coagulated wastewater, room temperature) 211

8-11 Adsorption isotherms for TOC (contact time = 1 h, pH = 8.5, wastewater after biological treatment, room temperature) 212

8-12 Scheme of a laboratory installation model for adsorption on activated carbon beds 213

8-13 Course of COD removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale 214

Number Page

8-14 Course of BOD removal on continuous adsorption process expressed as the average values of every 10 series, laboratory, scale 215

8-15 Course of color removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale 216

8-16 Course of detergent removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale 217

8-17 Residual COD concentrations according to carbon type and height of adsorptive column filling, laboratory scale 218

8-18 Residual BOD concentrations according to carbon type and height of adsorptive column filling, laboratory scale 219

8-19 Residual color concentrations according to carbon type and height of adsorptive column filling, laboratory scale 220

8-20 Residual detergent concentrations according to carbon type and height of adsorptive column filling, laboratory scale 221

8-21 Relation of COD adsorption rate to concentration in inflow, continuous process, laboratory scale 222

8-22 Relation of color adsorption rate to concentration in inflow, continuous process, laboratory scale 223

8-23 Scheme of installation for studies of adsorption in a continuous system, pilot scale 224

8-24 COD removal in continuous two stages of adsorption, series III 225

8-25 BOD removal in continuous two stages of adsorption, series III 226

8-26 Color removal in continuous two stages of adsorption, series III 227

8-27 Detergent removal in continuous two stages of adsorption, series III 228

8-28 COD removal in continuous three stages of adsorption, series IV 229

Number Page

8-29 BOD removal in continuous three stages of adsorption, series IV 230

8-30 Color removal in continuous three stages of adsorption, series IV 231

8-31 Detergent removal in continuous three stages of adsorption, series IV 232

8-32 Relation of rate of color and COD adsorption to concentration in inflow, continuous process on Z-4, series IV, pilot scale 233

8-33 COD removal in continuous adsorption on Z-4 carbon of various granulation, series V 234

8-34 BOD removal in continuous adsorption on Z-4 carbon of various granulation, series V 235

8-35 Color removal in continuous adsorption on Z-4 carbon of various granulation, series V 236

8-36 Course of COD removal from coagulated wastewater, pilot scale 237

8-37 Course of color removal from coagulated wastewater, pilot scale 238

Section 9

9-1 Scheme of ozonation apparatus on a laboratory scale, batch system 266

9-2 Change of absorption spectrum within the λ value. Range from 400 nm to 650 nm for the Salt of Naphthanil Blue BT dye in tap water solution in the course of ozone oxidation process. Ozone concentration in air = 12.7 mg/l, air flow = 18.6 l/h 267

9-3 Change of absorption spectrum within the λ value. Range from 400 nm to 650 nm for helanthrene green BS dye in tap water solution in the course of ozone oxidation process. Ozone concentration in air = 12.7 mg/l, air flow = 13.5 l/h 267

9-4 Dominant color removal depending on contact time of ozone oxidation for particular dyes in tap water solution 268

Number Page

9-5 Dominant color removal depending on contact time of ozone oxidation for particular dyes in biologically treated wastewater 269

9-6 Dominant color removal depending on contact time of ozone oxidation for five combinations of dyes in biologically treated wastewater 270

9-7 Dominant color removal depending on dye concentration for particular dyes in biologically treated wastewater 271

9-8 Amount of ozone consumed by sample depending on dye concentration for particular dyes in biologically treated wastewater 271

9-9 Relation between TOC and COD in ozone-treated wastewater with particular dyes added 272

9-10 Schematic flow diagram of cocurrent ozonation on a laboratory scale 273

9-11 Schematic flow diagram of one-stage countercurrent ozonation on a pilot scale 274

9-12 Removal of contaminants in a one-stage continuous countercurrent column using 10, 30, 50, and 70 mg/l ozone doses 275

9-13 Schematic flow diagram of double-stage ozonation on a pilot scale 276

9-14 Removal of contaminants in double-stage continuous columns using 10, 30, 50, and 70 mg/l ozone doses 277

Section 10

10-1 Scheme of ion-exchange system 327

10-2 Changes of anionic resin (Amberlite IRA-401) capacity in successive series 328

10-3 Percent color removal versus bed loading (BV/h) 329

10-4 Percent COD removal versus bed loading (BV/h) 330

10-5 Percent anionic detergent removal versus bed loading (BV/h) 331

10-6 Percent nonionic detergent removal versus bed loading (BV/h) 332

Number Page

Section 11

11-1 Schematic diagram of pilot plant at Andrychow for investigation of hyperfiltration process 419

11-2 Operating performance of cellulose acetate spiral wound membrane, model ROGA 4160 S 420

11-3 Color analyses of the first day sample 421

11-4 Color analyses of the second day sample 422

11-5 Color analyses of the third day sample 423

11-6 Color analyses of the fourth day sample 424

TABLES

Number **Page**

Section 4

4-1 Values of relative extinction at 450 nm and 500 nm for 10 wastewater samples treated biologically 29

4-2 Values of relative extinction at 450 nm and 500 nm for 10 wastewater samples treated by coagulation 30

4-3 Dye recovery on column with resin XAD-4 and percentage of dye retention on chromatographic column 31

4-4 Dye recovery on column with resin XAD-4 and percentage of dye retention on chromatographic column 34

4-5 Removal of dyes from wastewater by extraction 35

4-6 Eluting solvents for various groups of dyes 36

4-7 Column chromatography for dye mixtures in water and wastewater solutions 37

4-8 Column chromatography for dye mixtures in Table 4-4 38

4-9 Column chromatography for dye mixtures from dyehouse 38

4-10 Percent dye recovery from wastewater colored with various dye mixtures 39

4-11 Percent recovery from dyes isolated by extraction 39

Section 5

5-1 Consumption of dyes, chemicals, and auxiliary agents in the Andrychow cotton plant in 1976 57

5-2 Activated sludge process, pilot plant, first period 59

5-3 Influent and effluent wastewater quality at Andrychow mechanical-biological treatment plant. Studies carried out after October 10, 1975 60

Number Page

Section 6

6-1 Characteristics of filtration beds applied to investigations on laboratory scale, stage I 95

6-2 Effectiveness of the laboratory scale filtration process performed in the first stage of investigations 96

6-3 Characteristics of the filtration beds used for pilot plant investigations, stage II 100

6-4 Filtration bed values for column B 101

6-5 Effects of contaminant removal during filtration in pilot scale investigations, series I, stage II 102

6-6 Effects of contaminant removal during filtration in pilot scale investigations, series II, stage II 105

6-7 Effectiveness of the pilot plant filtration process performed in series III, stage II 107

6-8 Effectiveness of pilot scale filtration process based on average samples performed in series IV, stage II . . . 114

6-9 Results of physicochemical analysis in series V, stage II 117

6-10 Washing conditions of operation of a dual media filtration bed in relation to the cycle of filtration. Granulation of the bed according to the curve in figure 6-7, column B, series V, pilot scale 118

Section 7

7-1 Percent content of particular dye groups in total consumption of dyes in 1975 167

7-2 Color removal with 8 mg Cl_2/l 167

7-3 Residual dissolved aluminum after coagulation process . . . 168

7-4 Contaminant removal during filtration with simultaneous coagulation for higher pH (average results based on 16 days of operation) 169

7-5 Contaminant removal during filtration with simultaneous coagulation for lower pH (average results based on 24 days of operation) 170

Number Page

7-6 Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 10 days of operation) 171

7-7 Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 28 days of operation) 172

7-8 Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 36 days of operation) 173

7-9 Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 18 days of operation) 174

7-10 Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 14 days of operation) 175

7-11 Contaminant removal during filtration with simultaneous coagulation followed by oxidation with NaOCl and subsequent filtering (average results based on 14 days of operation) 176

7-12 Contaminant removal during coagulation in suspended flocs reactor followed by filtration (average results based on 26 days of operation) 177

7-13 Contaminant removal during coagulation in suspended flocs reactor followed by filtration (average results based on 10 days of operation) 178

Section 8

8-1 Physicochemical parameters of activated carbons 239

8-2 Results of studies of porous microstructure of activated carbons 240

8-3 Comparison of adsorption effects using three kinds of activated carbon, laboratory scale investigations 240

8-4 Physicochemical properties of activated carbons used in the regeneration process and of fresh carbons 241

Number | Page

8-5 Results of regeneration of Z-4, Calgon, and ARZ used in laboratory investigations by a continuous method . . . 242

8-6 Results of regeneration of Carbopol Z-4, spent in the two-stage adsorption process (AD_1 and AD_2) 243

8-7 Conditions of operation for activated carbon columns, pilot scale installation 244

8-8 Loads removed and final pollutant concentrations in individual series of adsorption on activated carbon, pilot scale installation 245

8-9 Characteristics of carbon beds and conditions of operation used for pilot scale adsorption of coagulated wastewater 246

8-10 Average removal of particular pollutants on activated carbon from coagulated wastewater at pilot plant 247

Section 9

9-1 COD determinations of dyes added to water and wastewater in laboratory investigations 278

9-2 Single dyes used in ozone oxidation investigations 279

9-3 Technical parameters and ozone balance in the ozone oxidation process of water dye solutions 280

9-4 Effectiveness of ozone oxidation of water dye solutions . . 283

9-5 Dyes fed into biologically treated wastewater 287

9-6 Effectiveness of ozone oxidation of biologically treated wastewaters with the addition of individual dyes and dye mixtures 288

9-7 Technical parameters and ozone balance in the ozone oxidation process applied to biologically treated wastewaters with the addition of individual dyes and dye mixtures 296

9-8 Technical parameters and ozone balance in the oxidation process applied to biologically treated wastewaters with the addition of individual dyes of different concentrations 299

9-9 Effectiveness of ozone oxidation of biologically treated wastewater with the addition of individual dyes of different concentrations 300

Number Page

9-10 Continuous cocurrent ozonation on a laboratory scale of biologically treated and filtered wastewater--ozone balance and contaminant removal 301

9-11 One-stage continuous countercurrent ozonation of biologically treated and filtered wastewater--ozone balance and color removal 305

9-12 One-stage continuous countercurrent ozonation of biologically treated and filtered wastewater--BOD_5, COD, and detergent removal 307

9-13 Double-stage continuous ozonation of biologically treated and filtered wastewater--ozone balance and color removal 310

9-14 Double-stage continuous ozonation of biologically treated and filtered wastewater--BOD_5, COD, and detergent removal 311

9-15 Comparative table of average values of percentage contaminant removal obtained by single-stage and double-stage ozonation 312

9-16 One-stage continuous ozonation of biologically treated wastewater after coagulation, filtration, and carbon adsorption processes--ozone balance and color removal . . 313

9-17 One-stage continuous ozonation of biologically treated wastewater after coagulation, filtration, and carbon adsorption processes--BOD_5, COD, TOC, and detergent removal 314

Section 10

10-1 Seven anionic and five cationic resins used in laboratory screening studies 333

10-2 Properties of different resins used in laboratory experiments 334

10-3 Dye-exchange capacity of resins used in laboratory experiments with reference to the best-absorbed dye . . . 335

10-4 Decrease in dye capacity after successive regeneration 336

10-5 Results of exchange capacity for wastewater investigations 337

Number Page

10-6 Characteristics of wastewater fed to the double ion-exchange system 338

10-7 Regenerator requirements for resins 339

10-8 The effectiveness of the single ion-exchange process with cationic and anionic resins (Amberlite IRA-401) at a bed loading of 6 BV/h (1 series) 340

10-9 The effectivness of the single ion-exchange process with cationic and anionic resins (Amberlite IRA-401) at a bed loading of 6 BV/h (2 series) 341

10-10 The effectiveness of the single ion-exchange process with cationic and anionic resins (Amberlite IRA-401) at a bed loading of 6 BV/h (3 series) 342

10-11 Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 6 BV/h 343

10-12 Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 12 BV/h 343

10-13 Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 18 BV/h 343

10-14 Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 6 BV/h 344

10-15 Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 12 BV/h 344

10-16 Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 18 BV/h 344

10-17 Percentage color removal from biologically treated wastewater with dyes of 50 mg/l concentration added, for different anionic exchange resins 345

10-18 Percentage of color removal from biologically treated wastewater with dyes of 60 mg/l concentration added, for different cationic exchange resins 346

10-19 Percentage of color removal from biologically treated wastewater without dyes added 347

10-20 Average percentage of COD removal in the ion-exchange process 348

10-21 Average percentage of anionic detergent removal in the ion-exchange process 349

Number Page

10-22 Average percentages of pollutant removal obtained in the ion-exchange process 350

10-23 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h (4 series) 351

10-24 The effectivess of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h (5 series) 354

10-25 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h (6 series) 356

10-26 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h (7 series) 359

10-27 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h (8 series) 362

10-28 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading 12 BV/h (9 series) 364

10-29 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading 12 BV/h (10 series) 367

10-30 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading 12 BV/h (11 series) 370

10-31 The effectivenss of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading 12 BV/h (12 series) 373

10-32 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h (13 series) 375

10-33 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 18 BV/h (14 series) 377

10-34 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 18 BV/h (15 series) . . 380

Number Page

10-35 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 18 BV/h (16 series) 383

10-36 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h (17 series) . . . 385

10-37 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h (18 series) . . . 387

10-38 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h (19 series) . . . 389

10-39 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h (20 series) . . . 391

10-40 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h (21 series) . . . 394

10-41 The effectivness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h (22 series) 397

10-42 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h (23 series) 400

10-43 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h (24 series) 403

10-44 The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h (25 series) 406

10-45 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401), at a bed loading of 6 BV/h during five successive series 408

10-46 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401), at a bed loading of 12 BV/h during five successive series 409

Number Page

10-47 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401), at a bed loading of 18 BV/h during three successive series 410

10-48 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 6 BV/h during three successive series 411

10-49 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 12 BV/h during three successive series 412

10-50 Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 18 BV/h during three successive series 413

10-51 Average values of pollutant removal for cation Zeolite 325 and anion Amberlite IRA-401 dual systems 414

10-52 Average values of pollutant removal for the cation Zeolite 325 and the anion Zeolite KMP system 414

Section 11

11-1 Preliminary test for ROGA membrane using 0.1 mol salt solution 425

11-2 Preliminary test for dynamically formed membrane using 0.1 mol salt solution 426

11-3 Operating conditions of the spiral wound cellulose acetate module (model ROGA 4160 S) during the wastewater test 427

11-4 Chemical analysis of the composite samples for entire test period 430

Section 12

12-1 Average effectiveness of the combined system for COD 433

12-2 Average effectiveness of the combined system for nonionic detergents 433

12-3 Effectiveness of individual processes applied after biological treatment 434

Number Page

12-4 Consumption of chemicals and materials and consumption volume of water wasted 435

12-5 Energy consumption and wastewater pumping head 436

ABBREVIATIONS AND SYMBOLS

ACP --Andrychow Cotton Plant
AD_1 --Carbon used in first stage of adsorption
AD_2 --Carbon used in second stage of adsorption
BOD_5 --Five-day biological oxygen demand
CC --Column chromatography
CEBEA --Chemical Industry Research and Development Center (Poland)
COD --Chemical oxygen demand
Co-Pt scale --Cobalt-platinum scale
EPA --Environmental Protection Agency (United States)
IGW --Water Economy Research Institute (Poland)
IMWM --Institute of Meteorology and Water Management (Poland)
LM --Methylene number
MG --Milligram number
Pt scale --Platinum scale for color
TLC --Thin-layer chromatography
TOC --Total organic content

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SECTION 1

INTRODUCTION

Work on project PR-5-532-3 began in 1972 in the then Water Economy Research Institute (IGW), Warsaw, Poland, in its Cracow Water Protection Section. The agreement between IGW and the U.S. Environmental Protection Agency was signed originally for the 3-year period from June 30, 1972, to June 29, 1975. The aim of the research was to determine the effectiveness and suitability of selected physicochemical technological processes for the thorough removal of color, detergents, and other refractory pollutants from textile wastewater, and to determine the most effective and economically feasible technological processes of tertiary treatment of combined textile and municipal wastewater, after conventional mechanical-biological treatment, for removing refractory substances and for bringing the wastewater quality up to a very high level.

Highly effective treatment of wastewater from the textile industry, which is one of the largest sources of strongly polluted wastewater, is becoming one of the most important requirements in small-stream catchment areas and, in particular, in areas deficient in water resources. Wastewater from the textile industry contains considerable amounts of substances that are wholly or partly resistant to treatment by biological means. As a result, textile industry wastewater that has been treated conventionally in a mechanical-biological plant cannot be put directly back into production, and if it is discharged into surface waters out of necessity, it causes deterioration of the qualitative indicators of the water. This deterioration stems especially from such refractory substances as dyes, detergents, and other synthetic compounds used in the textile industry. These constitute a special problem when the receiving stream is small and high water quality must be maintained because the watercourse or stream is used as a supply source for domestic purposes. The further expansion of the textile industry will make the situation in water administration worse; therefore, it is necessary to study more effective methods of tertiary treatment of textile wastewater now.

This study set out to check the effectiveness of technological processes of third-stage treatment for removal of refractory substances, in particular, color, COD, and detergents. The investigations were planned first on a laboratory scale, and then on a large laboratory scale at the pilot plant in Andrychow. Studies were made of a series of physicochemical processes applied to wastewater after mechanical-biological treatment. These studies included:

- Rapid filtration on single and multi-media beds,
- adsorption on granular activated carbon,
- ion exchange on anionic and cationic resins,
- coagulation with the use of typical coagulants and with the application of auxiliary chemicals,
- oxidation with ozone and chloride, and
- reverse osmosis.

The research program was designed to examine these processes both individually and in combination in a linked technological system.

The research work began with investigations on a laboratory scale. At the same time, the construction of a pilot plant was begun at the municipal-industrial sewage treatment plant at Andrychow. As a result of delays in the construction and completion of the pilot plant equipment, and in particular, on account of difficulties in purchasing equipment for reverse osmosis, the project completion date was postponed for another 2 years to June 29, 1977. Meanwhile, as a result of reorganization in 1973, the Water Protection Section in Cracow was transferred to the new Institute of Meteorology and Water Management, which administered the project until its completion.

SECTION 2

CONCLUSIONS

1. The concept of applying biological treatment before physicochemical tertiary treatment has proved valid for mixed textile and municipal wastewater in a proportion varying from 1:1 to 2:1. Activated sludge that decomposes a considerable load of organic pollutants relieves the physicochemical processes and to a large degree levels out the flow variation and variable composition of the wastewater. As a result, smaller quantities of chemicals are needed for coagulation and oxidation, and less activated carbon is consumed in the adsorption process, making the operation of the physicochemical processes more certain and their control easier. Activated sludge also increases the effectiveness of organic load removal for the whole treatment system.

2. The optimum system of tertiary treatment that brings the quality of the treated wastewater up to class I water purity (appendix C) and allows for possible reclamation of water for the supply of different utilities is as follows:

   - Contact coagulation with aluminum sulphate on upstream filters possibly preceded by chlorination,
   - filtration on a two-layer anthracite-sand bed, and
   - adsorption on activated carbon.

3. The investigations show that, where very effective biological treatment of wastewater is needed, rapid sand filtration can be recommended as either a final or an intermediate process applied before other tertiary physicochemical processes such as adsorption, ion exchange, or hyperfiltration. The filtration itself reduces the concentration of suspended solids to below 10 mg/l, which results in 30 to 75 percent removal of BOD_5 load.

4. A dual media bed is more effective for filtration of biologically treated wastewater than a single medium bed. A dual media bed ensures better elimination of suspended solids and a filtration cycle of 23 to 36 h, in contrast to the 3.5 to 23.5-h filtration cycle obtained with a single medium bed.

5. The increase of the filtration rate up to 15 m^3/m^2h diminishes the effectiveness of the bed because the removal of contaminants becomes less regular, especially in the case of beds having very finely granu-

lated filtration media. A filtration rate of 8 m^3/m^2h has been found to be the optimum for the Andrychow municipal-textile wastewater.

6. The method of contact coagulation with simultaneous upflow filtration lends itself more to the coagulation of biologically treated wastewater than does the conventional coagulation performed in a reactor with suspended flocs. Before the coagulation process, preliminary treatment is necessary for pH control and efficient removal of organics in the activated sludge process to prevent secondary pollution of the wastewater by aluminum compounds developing in the solution.

7. Adsorption on activated carbon ensures removal of a broad range of refractory pollutants from biologically treated, mixed textile industry and municipal wastewater. The effectiveness of treatment depends on the appropriate choice of activated carbon and process parameters. Activated carbons with large pore volumes should be used for treating wastewater with a high concentration of pollutants. Such a carbon is Carbopol Z-4. But where thorough removal of pollutants is necessary, carbons with a large adsorptive surface having many tiny pores (<1,500 Å) should be chosen. Among such carbons are Hydrodarco and Calgon.

8. Adsorption on activated carbon applied to wastewater after biological treatment and coagulation will remove approximately twice the percent of specific refractory pollutants compared to removal from biologically treated, noncoagulated wastewater. Percentage removal of typical parameters was: COD and color--more than 80 percent; TOC--65 percent on the average. The combination of adsorption with coagulation is the best method of practical application.

9. Ozone oxidation of previously biologically treated wastewater is an effective process, especially for color removal, which approaches 67 percent, and for removal of anionic detergents, which approaches 100 percent. Removal of organic compounds designated as COD occurs slowly (32 percent removal) and with a large ozone demand represented by a dose of 50 mg/l with a 30-min contact time. The application of ozone oxidation during the last stage of the combined tertiary treatment system after adsorption proved to have little effect.

10. The ion-exchange process is effective for removing color and anionic detergents. However, the disadvantages of this process--a short work cycle (6 to 20 h), a long regeneration time, a large amount of post regeneration waters with a large pollutant load, and the cost of resins--render it unsuitable for use with mixed municipal and textile wastewater.

11. The research on the hyperfiltration process should be treated as preliminary and as a guide. It was carried out mainly in order to compare its effects with those of other tertiary treatment processes. The effectiveness of hyperfiltration in the reduction of color and dis-

solved substances is satisfactory. There remains, however, the unsolved problem of the concentrate, which in the case of mixed textile and municipal wastewater requires additional treatment. The application of this process to isolated textile wastewater from the dyeing and cloth-finishing processes is promising because of opportunity utilization of both product water and concentrate.

12. As has been shown in the hyperfiltration tests so far, thorough preliminary removal of fine suspended solids and colloids from wastewater is of essential significance to prevent flocs decline, fouling, and module damage due to clogging. This is particularly important when spiral wound membranes are applied to biologically treated mixed wastewater.

13. The application of thin-layer and column chromatography for analysis of color substances in biologically treated combined municipal and textile wastewater appeared not to be useful because the concentration of dyes was too low to yield a clear chromatogram. However, the above-mentioned methods, particularly the column chromatography combined with preliminary separation of dyes on XAD-4 resin, can be useful for the quantitative analysis of dyes in concentrated wastewater from a dyeing house.

SECTION 3

RECOMMENDATIONS

Research should be continued on the process of hyperfiltration (reverse osmosis) of isolated textile wastewater from the dyeing and cloth-finishing processes.

In the light of research already completed, the application of hyperfiltration to the treatment of mixed textile and municipal wastewater is at present technically and economically unsound, mainly because there is no way to make use of the concentrate. It would be appropriate to undertake research to determine the technological properties and optimum technology for the treatment and possible utilization of sludge and concentrates produced in the individual physicochemical processes studied.

Processes for treating sediments and byproducts have a large, and in some cases, a deciding influence on the costs of tertiary treatment processes.

For purposes of reclaiming treated combined textile and municipal wastewater for supply to different utilities, bacteriological composition is very important. Further research on what has been determined to be the optimum tertiary treatment system (coagulation, filtration, and adsorption) should take into account the removal of bacterial pollutants.

It is also advisable to examine in more detail the influence of the method and degree of biological treatment on the parameters and economics of tertiary treatment of mixed textile and municipal wastewater.

There is a need for further pilot investigations into oxidation, using both chlorine and oxygen from air with the help of different catalysts such as ultraviolet light.

SECTION 4

PROCEDURE AND ANALYTICAL RESEARCH

ANALYTICAL PROCEDURE

Daily composite samples of the wastewater from each particular unit process were collected from influent and effluent for analysis. When a continuous process was involved, average samples were collected proportionally to flow during a day or cycle of operation. In addition, grab samples were taken occasionally in order to study the course of the process during a cycle of operation.

The basic analytical determination applied in each process comprised the following indicators:

- pH reaction--according to the standard methods [1];
- alkalinity--according to the standard methods;
- acidity--according to the standard methods;
- suspended solids--according to the standard methods [1,2];
- permanganate COD--according to the procedure described in appendix A [2];
- dichromate COD--according to the standard methods [1];
- BOD_5--by standard dilution technique [1];
- anionic detergents (ABS)--with the methylene blue method [1,2];
- nonionic detergents--according to the procedure described in appendix A;
- color--by three methods:
    1. spectrophotometrically, by light absorption measurement within the range of wavelengths 360 to 650 nm (the average absorption value has been calculated from 10 measurements on the absorption curve divided into 10 equal sections);
    2. color threshold; and
    3. color related to Pt scale.

In the investigations of individual processes some other analytical determinations have been made:

- Aluminum content--according to the procedure described in appendix A;
- conductivity--with conductivity meter;
- ozone--by iodometric method [1];
- turbidity--according to the standard procedure [2]; and

- total organic carbon--with Beckman apparatus.

In the above-listed analysis, special attention has been given to the color measurements and separation. The following subsections deal with this problem.

TEST INVESTIGATIONS ON THE SPECTROPHOTOMETRIC DETERMINATION OF COLOR

Colored substances from the Andrychow Cotton Plant (ACP) are among the main pollutants of the wastewater under investigation. Therefore, a quick and reproducible method of determining color is necessary to make it possible to determine changes in the colored substance content of wastewater subjected to different treatment processes.

The Lambert-Beer law defines the basic dependence between the absorption of light and the concentration of colored substances in the solutions by the equation:

$$A = ECl$$

where:

A = extinction,

E = absorption coefficient,

C = concentration of substance absorbing the light, and

l = thickness of the fluid layer.

For solutions that, like the wastewater under investigation, contain more than one dissolved substance:

$$A = \Sigma A_i = l \times E_i \times C_i \ .$$

Assuming that the average absorption coefficient appears in wastewater, extinction is proportional to the concentration of colored substances in the solution. The absorption spectra are described by similarly shaped curves moved with regard to the axis on which the extinction values are plotted. On the basis of this calculation, the rate of decrease of extinction which can be measured for one wavelength, or as an average value for several wavelenghts, is directly proportional to the concentration of dyes.

Tests to establish the accuracy of determining color in Andrychow wastewater by spectrophotometrical measurement were carried out on 10 samples of wastewater after biological treatment and on 10 samples after coagulation. Spekol and Specord spectrophotometers produced by Carl Zeiss Jena were used for spectral analysis. Cuvettes 5 cm long were used. The analysis showed relatively large extinction values in the range from 400 to 500 nm; these were accepted as authoritative for further investigations. At wavelengths greater than 500 nm the extinctions were small (below 0.05), and within the error range of the apparatus. The spectrum of the studied samples of wastewater was a continuous function. If the shapes of the curves illustrating the dependence of extinction on the wavelength are identical for the different samples, then the ratio of extinction values for two arbitrarily chosen wavelengths on the curves in question should be constant.

Some calculations were performed as examples by taking extinction for 400 nm as equal to 1: for $\lambda = 450$ nm, the extinction value = A'; and for $\lambda = 500$ nm, the extinction value = A''. Thus, relative extinction can be expressed as:

$$X_1 = \frac{A'}{A} \quad \text{and} \quad X_2 = \frac{A''}{A} \quad .$$

The results for 10 wastewater samples after biological treatment and coagulation are presented in tables 4-1 and 4-2.

The results obtained were evaluated statistically as follows:

Wastewater samples after biological treatment:

For 450 nm:

$$\sum_{i=1}^{10} X_i = 5.02$$

$$\text{mean value of } X, \ \overline{X} = 0.50$$

$$\Sigma(X_i-\overline{X})^2 = 0.0374 \quad .$$

Standard deviation (S) of a single result is:

$$S = \sqrt{\frac{(X_i-\overline{X})^2}{n-1}} = \sqrt{\frac{0.0374}{9}} = 0.064.$$

Dispersion of the results characterized by the coefficient of variance (V) is:

$$V = \frac{S \times 100}{\overline{X}} = \frac{0.064 \times 100}{0.50} = 12.8\% \ .$$

For 500 nm:

$$\sum_{i=1}^{10} X_i = 3.76; \qquad \overline{X} = 0.38$$

$$\Sigma(X_i-\overline{X})^2 = 0.0267$$

$$S = \sqrt{\frac{0.0267}{9}} = 0.054$$

$$V = \frac{0.054 \times 100}{0.38} = 14.2\%$$

Wastewater Samples After Coagulation:

For 450 nm:

$$\sum_{i=1}^{10} X_i = 4.99; \quad \overline{X} = 0.50$$

$$\Sigma(X_i-\overline{X})^2 = 0.0421$$

$$S = \sqrt{\frac{0.0421}{9}} = 0.068$$

$$V = \frac{0.068 \times 100}{0.50} = 13.7\% .$$

For 500 nm:

$$\sum_{i=1}^{10} X_i = 3.61; \quad \overline{X} = 0.36$$

$$\Sigma(X_i-\overline{X})^2 = 0.0249$$

$$S = \sqrt{\frac{0.0249}{9}} = 0.052$$

$$V = \frac{0.052 \times 100}{0.36} = 14.5\%$$

The results show that the curves of dependence of extinction on wavelength for biologically treated and coagulated wastewater have similar shapes. However, the dispersion of results is considerable--from 12 to 14.5 percent. In connection with the above, the possibility of determining color by summary extinction for the wavelengths 400, 450, and 500 nm is calculated: for λ = 400 nm, A was determined = 1; for λ = 450 nm, A_i was determined = X_{i1}; and for λ = 500 nm, A_2 was determined = X_{i2}; taking the quotients:

$$X_{i1} = \frac{A_1}{A} \text{ and } X_{i2} = \frac{A_2}{A}$$

$$A+A_1+A_2 = A(1+X_{i1}+X_{i2}).$$

For the previously analyzed values contained in tables 4-1 and 4-2, it was calculated that:

For biologically-treated wastewater:

$$\sum_{i=1}^{10} X_i = 18.78; \quad \overline{X} = 1.88$$

$$\sum_{i=1}^{10} (X_i - \overline{X})^2 = 0.0806$$

$$S = \sqrt{\frac{0.0806}{9}} = 0.095$$

$$V = \frac{0.095 \times 100}{1.88} = 5.05\%;$$

For coagulated wastewater:

$$\sum_{i=1}^{10} X_i = 18.60; \quad \overline{X} = 1.86$$

$$\sum_{i=1}^{10} (X_i - \overline{X})^2 = 0.0978$$

$$S = \sqrt{\frac{0.0844}{9}} = 0.104$$

18

$$V = \frac{0.104 \times 100}{1.86} = 5.6\% .$$

From the above calculation it is clear that, through the determination of summary extinction, lesser coefficients of variations amounting to about 5 percent are obtained. Therefore, it is valid to accept values of summary extinction or the average extinction of the chosen wavelength range of the spectrum for comparison of wastewater color.

To check whether the decrease in concentration of colored substances follows the Lambert-Beer law, an experiment was carried out in which a sample of wastewater was diluted with distilled water in the ratios of 1:3, 1:1, and 3:1.

In the diluted samples extinction was determined for three wavelengths. Taking the initial extinction value as equal to 1, relative extinction was calculated respectively for individual dilutions and wavelengths. The results are plotted in figure 4-1. From these it is clear that the dependence between extinction and dilution is a straight line. So reduction of extinction is directly proportional to a decrease in the amount of color substances in the wastewater.

ATTEMPTS AT CHROMATOGRAPHIC IDENTIFICATION OF DYE SUBSTANCES

Subject and Scope of Investigations

On account of the significance dye substances and the color they produce have in textile wastewater, it was necessary to carry out additional investigations to assess the possibilities of more precisely identifying those dye substances and of determining the effectiveness of wastewater treatment processes. For this purpose, methods of column chromatography (CC) and thin-layer chromatography (TLC) were used. These methods are used in many fields of chemical technology to separate and treat substances, to isolate them for solutions or mixtures, and to make qualitative and quantitative determinations of dyes. The investigations were carried out by choosing the chromatographic system which would best allow for separation and identification of dye compounds at different concentrations in textile wastewater. The work was begun with a chromatographic analysis conducted on thin-layer plates covered with silica gel, cellulose, or aluminum oxide. Then the column chromatography method was applied and performed in parallel with the thin-layer method.

The following dye samples were used for chromatographic analyses:

- Dyes in pure water solutions--0.5%,
- dyes added to biologically treated wastewater,
- wastewater before and after the ion-exchange process,
- mixed textile and municipal wastewater after biological treatment with variable color: weak and intense color,
- wastewater before and after the ozonation process, and
- wastewater collected directly from the fabric-dyeing house.

The following dyes used currently in the ACP [1, 6, 2] were used for the investigations.

Sulfur Dyes

Sulphur Khaki G (C.I. Sulphur Green 8:1)*
Sulphur Black WT (C.I. Solubilised Sulphur Black 1; 53186)

---

*Where possible, the manufacturer's name for each dye is followed in parentheses by the Colour Index generic name and constitution number. Both generic names and constitution numbers are absent for commercial dye names not listed in the Colour Index, third edition. Some dyes listed in the Colour Index are assigned generic names only; their constitution numbers have not been determined.

Vat Dyes:

Helanthrene Green BS
Helanthrene Olive BT

Indigosol Dyes:

Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106)
Helasol Grey BL (C.I. Solubilised Vat Black 1; 73671)

Helasol Orange RK (C.I. Solubilised Vat Orange 3; 59301)
Helasol Pink R (C.I. Solubilised Vat Red 1; 73361)

Reactive Dyes:

Helaktyn Yellow DGR
Helaktyn Yellow D5GN
Drimarene Green X-2BL (C.I. Reactive Green 15)
Remazol Brilliant Blue (C.I. Reactive Blue 19; 61200)
Helaktyne Red F5B

Dispersed Dyes:

Synten Rubine P-3B (C.I. Disperse Red 5; 11215)
Synten Navy Blue P-BL
Indanthren Bordeaux RR (C.I. Vat Red 15; 71100)
Synten Azure
Synten Yellow 5G (C.I. Disperse Yellow 5; 12790)

Glacial Dyes:

Natural Azure Salt BT

The scope of investigations included introductory operations intended to isolate dye compounds from solutions. After the introductory operations the actual chromatographic analysis was begun with the thin-layer and column methods, a suitable kind of plate, suitable chromatographic column material filling, and the best solvents.

Method and Course of Investigations

Introductory Processes--

Before chromatographic analysis began, samples were subjected to various introductory processes such as concentration by evaporation, retention of dyes on column with ion-exchange XAD-4 resin [3], and extraction of retained dyes with organic solvents [4].

Condensation of samples--In the first stage of investigations the method of concentration by evaporation was used [5]. After evaporation of 2 or 3 l of wastewater, about 2 to 5 ml of concentrate with an intense coloring was obtained. The concentrate thus obtained was subjected to chromatographic analysis on thin-layer plates. It was found that the concentration method can be applied to solutions when they are more intensely colored. In the majority of samples studied, concentration by evaporation caused the wastewater to pass to a semiliquid consistency before it reached a color concentration that left distinct spots on the plates.

Further tests of concentration by evaporation were abandoned, since this method was found to be unsuitable.

Retention of dyes on ion-exchange resins--The ion-exchange bed was formed by the resin XAD-4, which is polystyrene and bivinylbenzene copolymer with low polarity and pore diameter of 50 Å [6]. Before investigations were started, this resin was adequately cleaned in a Soxlete apparatus by the extraction method using methanol once and ethyl ether twice. Extraction was carried out in each solvents for 8 h. After cleaning, the resin was kept in methanol in order to guarantee a large active surface.

The test with ion exchange was conducted in glass columns 50 cm high and 2.5 cm in diameter. The height of the bed was 20 to 30 cm. The resin layer in the form of suspended matter was placed in methanol on porous glass covered with a glass wool plug. A glass wool plug was also placed above the resin. Before investigations began, the methanol was removed and the bed was washed with 20 ml of distilled water. Dye solutions, as described in table 4-3, were fed onto the XAD-4 bed from above. Dyes, as compounds containing chromophor and auxochrome groupings that determine their usefulness and color, have the capacity to exchange those groupings with ions in the bed. Samples of dye solutions were subjected to spectrophotometric analysis both before they were fed to the column in quantities of 40 ml and after they left the column. Their transmission was determined in the range of visible light from λ = 420 to 650 nm for every 10 units.

The results obtained in relation to wavelength were presented on diagrams from which the value of the dominant λ was determined. For the value of the dominant λ, determined as a distinct peak, the percentage of dye retained was calculated [6]. In the case of graphs which did not contain distinct peaks, average results of determinations of transmission were taken from individual divisions.

After the dye had been washed with a constant portion of ethyl ether (15 ml), the column with the resin was subjected to regeneration [7]. Thirty ml of methanol were added, then removed after 10 minutes contact with the resin. The resin column was filled again with fresh methanol and plugged.

The results of investigations from the dye compound retention process set out in tables 4-3 and 4-4. On the basis of these results we can conclude that all the dyes examined were isolated from water solutions to a considerable degree [figure 4-2]. The highest percentage of retained dyes--on the average 88.2 percent--was observed for reactive groups, and the lowest--18.6 percent--for vat dyes (sulfur--18.3 percent; indigosol--81.3 percent) [figures 4-4, 4-5, and 4-6].

Extraction methods--In addition to the ion-exchange method, the process of extraction was also used to isolate color compounds from solutions. Extraction is the process of the transfer of a defined chemical substance, dissolved in a fluid phase, to another fluid phase that is not mixed with the first. In the present investigations, a mixture of the following solvents constituted an organic liquid phase: isopropyl alcohol: alcohol n-butyl:ethyl octane in the ratio 30:50:20.

This method was applied to both natural biologically treated wastewater colored with a constant amount of dye (5 mg/l), and to natural noncolored wastewater. The dyes were extracted in a 100-ml mixture of the above solvents, as evidenced by the increase in the color intensity of the solvent layer. For natural noncolored wastewater, extraction was performed from 5 l of wastewater. The percentage of transmission of the organic bed in the range of visible light was determined. The results are set out in table 4-5.

On the basis of these results, it appears that the extraction method, the purpose of which is to isolate color compounds, does not yield high percentages of extracted dyes. As a result, this method was discontinued, and the method of retaining dyes in the column with the resin XAD-4 was accepted as the main preliminary method for isolation of dye compounds from solution.

Chromatographic Analysis--

Thin-layer chromatography--In the investigations carried out into the separation of dyes contained in textile wastewater, the thin-layer chromatography method was first used with the application of plates covered with silica gel, aluminum oxide, and cellulose [8,9]. In the first stage of investigations a series of preliminary tests were carried out with the aim of choosing suitable thin-layer plates and eluting solutions appropriate for the given dye groups. Plates covered with silica gel were chosen as the best ones. The eluting solvents for the individual groups of dyes are listed in table 4-6.

A drop of the examined mixture of two or three dyes, isolated from the wastewater by the method of ion exchange on resin XAD-4, was deposited on the thin-layer plate. The dyes were washed in 15 ml of ethyl ether. A drop of the mixture under examination was placed on the starting line, and the plate was placed in a closed vessel with its edge immersed in the chromatogram-developing solvent.

Thin-layer chromatography analysis was also used for color compounds isolated from biologically treated natural wastewater after it had been condensed and the color retained on the resin layer. Dyes coming directly from the dyeworks wastewater were also subjected to this analysis. After chromatograms had developed, individual spots of color, together with the silica gel, were separated from the bed. The color was washed out with the solvents specified and was determined spectrometrically. On the basis of the transmission percentages obtained, the recovery of the corresponding dyes were determined.

Column chromatography--When investigations into the separation of color compounds were being expanded, the column method was introduced. Dyes isolated from the following solutions [10] were subjected to separation on the chromatographic column:

- Water solutions of dye, 5 mg/l;
- biologically treated wastewater colored with dye, 5 mg/l;
- biologically treated wastewater with a moderate natural color;
- biologically treated wastewater with an intense specific coloring;
- biologically treated wastewater additionally colored with mixtures (I to V in table 4-4) 50 mg/l before and after the ozonation process;
- wastewater collected directly from the cloth-dyeing department.

The dyes were isolated from the solutions on the column with the resin XAD-4. Two to three ether solutions of washed-out dyes were mixed in the ratio 1:1 and were fed onto the chromatographic column from the top.

Given in tables 4-7, 4-8, and 4-9 are the solvents and chromatographic column fillings used in relation to dyes isolated from water, wastewater, wastewater mixtures before and after ozonation, and dyehouse process streams. Examples of the spectrographic analysis showing the separation of these dyes by the column chromotographic process are provided in figures 4-7 and 4-8.

Column chromatography was also applied to investigations into the separation of color compounds coming from natural wastewater collected from the biological treatment effluent. The chemical compounds given above and the solvents which develop the chromatogram were used as a carrier (mobile phase).

After color compounds were isolated from the wastewater by the extraction method, worse dye isolation results were obtained. (figure 4-9) As a result of this, investigations of column chromatography in application to these compounds were limited to tests of biologically treated wastewater synthetically colored with 5 mg/l of dye, and of natural wastewater collected from the activated sludge process effluent. After the color compounds had passed to the solvent bed, which was composed of isopropyl alcohol:n-butanol:ethyl octane (30:50:20), the transmission of this bed in the range from 420 to 650 nm was examined. The solution was condensed to 20 ml and the chromatogram was developed on the silica gel.

Results of Investigations--

Thin-layer chromatography--The percentage dye recovery from wastewater samples synthetically colored with a mixture of two dyes was as shown in the table on the following page.

These dye recovery percentages are considerably lower than those obtained by the column method for the same dyes. For example, Helanthrene Green BS showed 15.3 percent dye recovery from the thin-layer plate and 32.5 percent recovery with the chromatographic column method; Helasol

Pink R showed 12.0 percent recovery from the thin-layer plate and 40.4 percent recovery with the chromatographic column method.

When chromatographic analysis performed on thin-layer plates was used in relation to natural wastewater, no positive results were obtained. When thin-layer plates were applied to natural wastewater after activated sludge, a legible chromatogram was not obtained because the spot was uniform, blurred, and yellowish. In this case, the methods of condensation [11] and ion-exchange resin XAD-4 were used simultaneously as introductory processes.

Column chromatography--The results of separation of color compounds on the chromatographic column are given in tables 4-3 and 4-4. The dyes subjected to chromatographic analysis were isolated from the solutions by the method of ion exchange on resin XAD-4 [12,13].

On the basis of the results the following conclusions can be drawn:

1. The dye recovery percentages quoted in table 4-3 indicate that the column chromatography method is suitable for solutions with a color compound content greater than 5 mg/1.
2. Table 4-4 indicates that the highest percentages of recovery of color compounds were obtained for the dyes Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106) (96.0 percent) and Drimarene Green X-2BL (C.I. Reactive Green 15) (86.5 percent).
3. A high level of dye recovery was also obtained for wastewater collected directly from the cloth-dyeing department and for the solutions used in the ozonation processes for the first four mixtures. The dye recovery levels following the ozonazation process are lower than those preceding it. However, for wastewater of a lower color concentration, the column chromatography method did not yield the expected degree of recovery.
4. In chromatographic studies carried out by the column method on natural wastewater, from which refractory substances had been isolated by concentration and by ion exchange, successively, a separation of dyes was not obtained for any of the carrier substances mentioned.
5. For wastewater containing a characteristic blue-green coloring, after the separation of color compounds on resin, a blurred chromatogram without clearly defined color bands was obtained on the chromatographic column. A measurement of transmission in this case was impossible. In investigations of wastewater condensed from 5 1 to 1 ml with a specific green-blue color, a uniform blue band was obtained on the chromatographic column. The dye recovery here was 7.2 percent.
6. The development of a chromatogram composed of dyes isolated from solutions by the extraction method resulted in blurred color bands, which were difficult to separate at an intensity less than that after ion exchange. The percentage dye recovery on the column in this case was as shown in table 4-11.
7. In investigations carried out on wastewater with a natural color, a uniform, blurred band, like that in the previous investigations, was obtained on the column.
8. For wastewater with characteristic coloring after initial condensation and extraction, a uniform band was obtained on the column. The color recovery percentages--3.5 percent, 4.8 percent, and 2.3 percent, suc-

cessively--average 3.9 percent. This result has no practical significance.

Discussion of the Results of Investigations--

On the basis of the chromatographic investigations carried out with the aim of isolating, separating, and possibly identifying the color compounds contained in wastewater from the textile industry, we conclude that chromatographic analysis cannot be applied to biologically treated wastewater because the color concentration is too small to yield legible chromatograms either in the chromatographic column or on thin-layer plates.

Another reason for the unsuitability of the column chromatography method in application to wastewater collected at the pilot plant in Andrychow is the presence of various other organic compounds, such as phenols, which influence the disintegration of the dye structure and cause the formation of other compounds in conjunction with particles of dye. Therefore, identification is impossible, as is a comparison with model chromatograms.

The same conclusion applies to additionally colored wastewater in which the presence of other, mainly organic, compounds has a negative influence on a legible chromatogram, although the content of the dyes added may be sufficient--that is, there may be good division and recovery percentages, but difficulties with the identification of compounds.

Column chromatography appears to be a suitable method for wastewater collected directly from the dyeing processes in which the concentration of color compounds is high and the amount of other organic pollutants is relatively low.

Conclusions

1. TLC and CC methods are not useful for color analysis of biologically treated wastewater samples collected after physicochemical treatment processes. The concentration of dye compounds is not high enough to produce a clear chromatogram. For color analysis, the minimum concentration of dye compounds in wastewater necessary to insure a correct chromatographic analysis is 5 mg/l. Before applying chromatographic methods of analysis it is necessary to separate dye compounds from their wastewater or water solutions and transfer them to the organic layer by means of ion-exchange processes.

2. As a result of the high content of dissolved salts and the required high degree of concentration of the dye compounds, concentrating those compounds by evaporation brought no positive results. The mixture became semiliquid before a concentration of dyes capable of producing distinct bands of color could be obtained.

3. Two essential factors are the choice of the proper adsorbent or the right type of thin-layer plate, and the choice of a developing phase for the particular group of dye compounds.

4. The column and thin-layer chromatography can constitute the techniques for separating and controlling the recovery of the dye compounds from the wastewater sample collected directly from the textile-dyeing department.

5. The presence of other organic compounds in wastewater, such as phenols, for the most part exerts an unfavorable influence on the chromatographic pattern and causes the displacement of bands and changes in the color intensity in comparison to the standard solutions.

6. The investigations showed that chromatographic analysis performed on thin-layer plates can be applied to qualitative determinations of the compounds. But for quantitative determinations, this method proved unsuitable due to the inaccuracy of results arising during the mechanical removal of gel from the base. In quantitative investigations the column method gave good results.

7. The quantitative determinations carried out lead to the conclusion that the recovery of the dyes has been determined within an error range of about 15 percent.

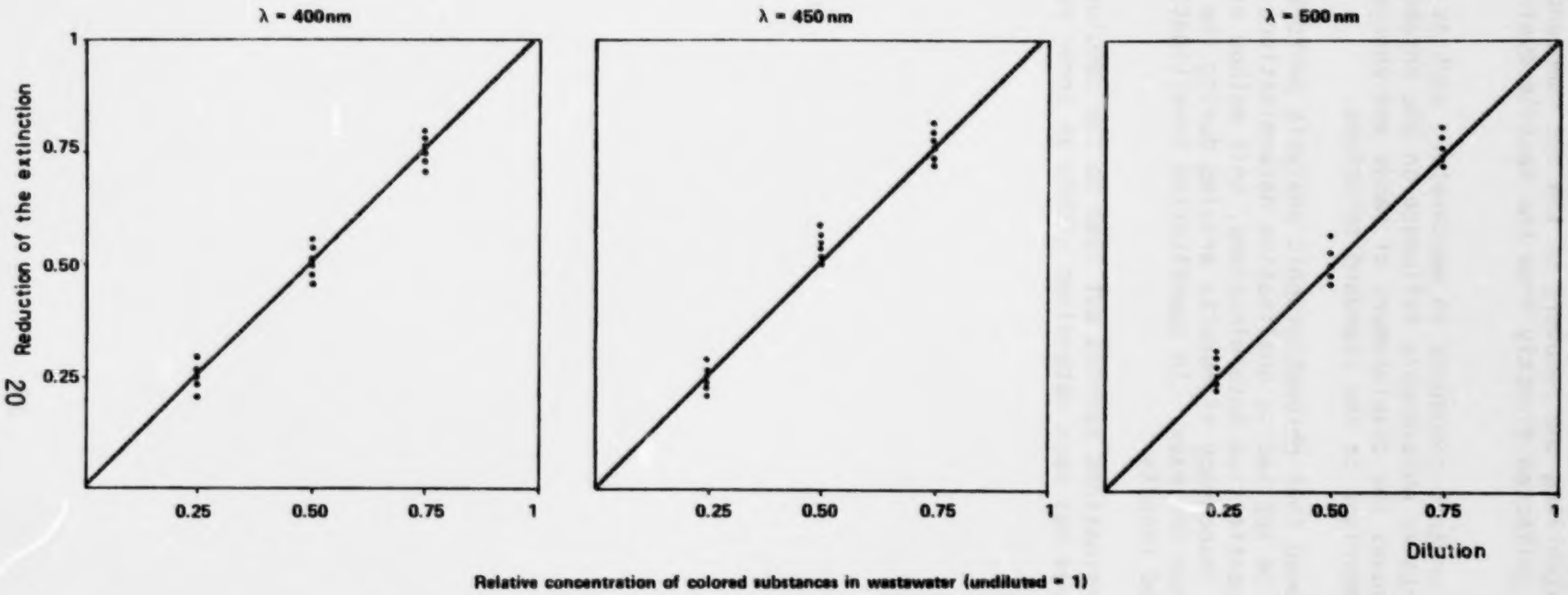


Figure 4-1. Dependence between the reduction of the extinction and the wastewater dilution for various wavelengths.

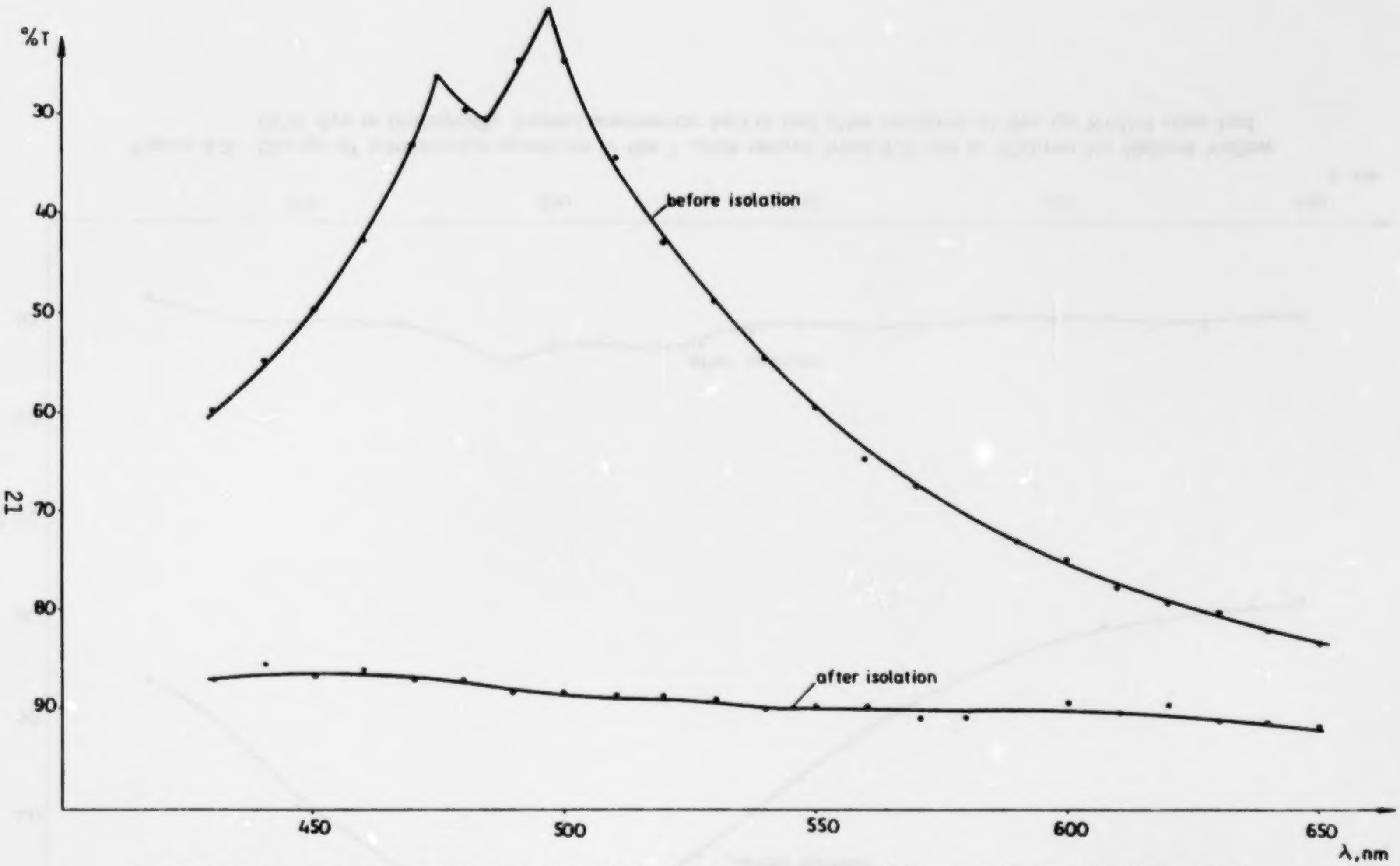


Figure 4-2. Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for Helasol Yellow GOK dye in water solution before and after isolation of dye on XAD-4 resin bed.

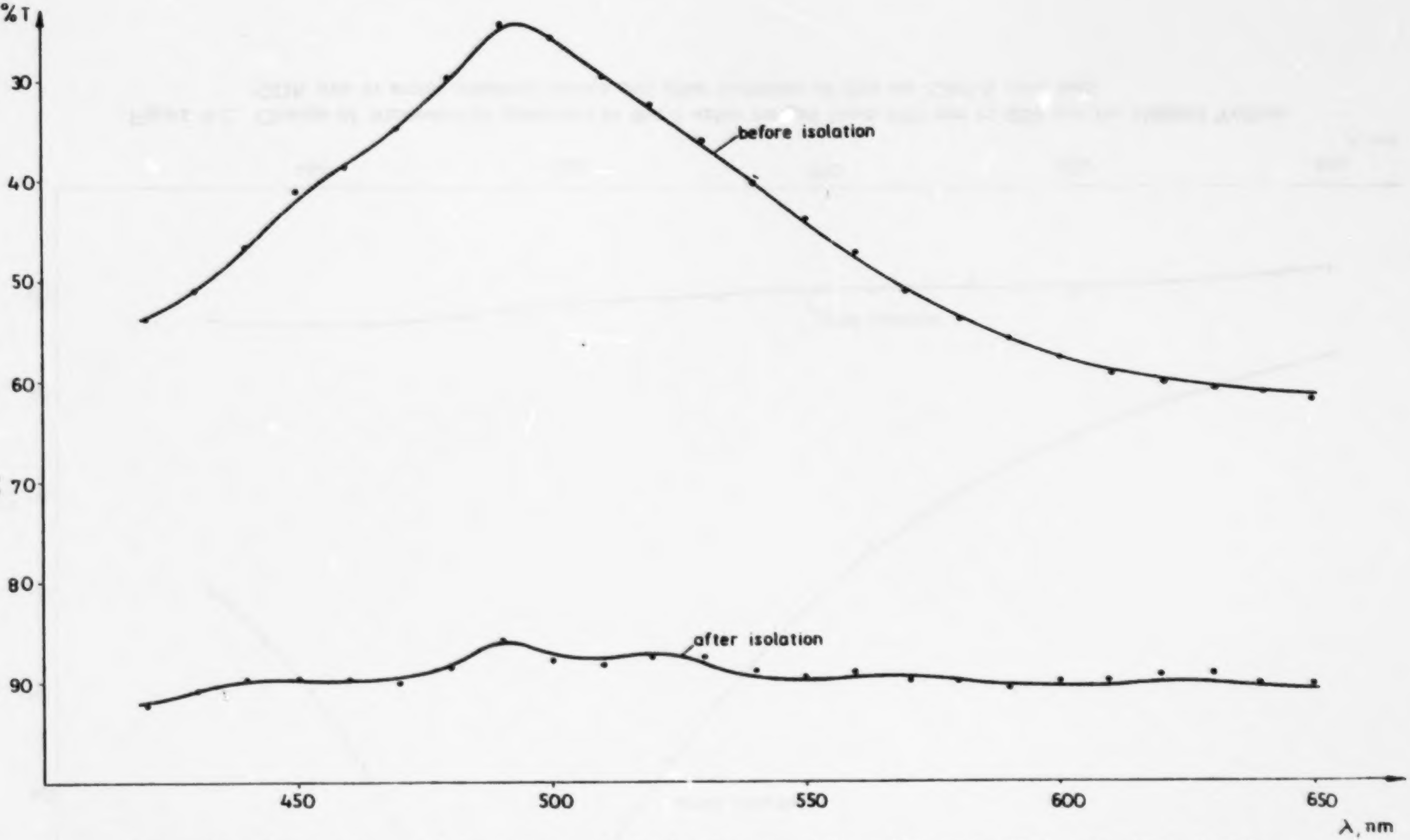


Figure 4-3. Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for Helasol Yellow GOK dye in biologically treated wastewater before and after isolation of dye on XAD-4 resin bed.

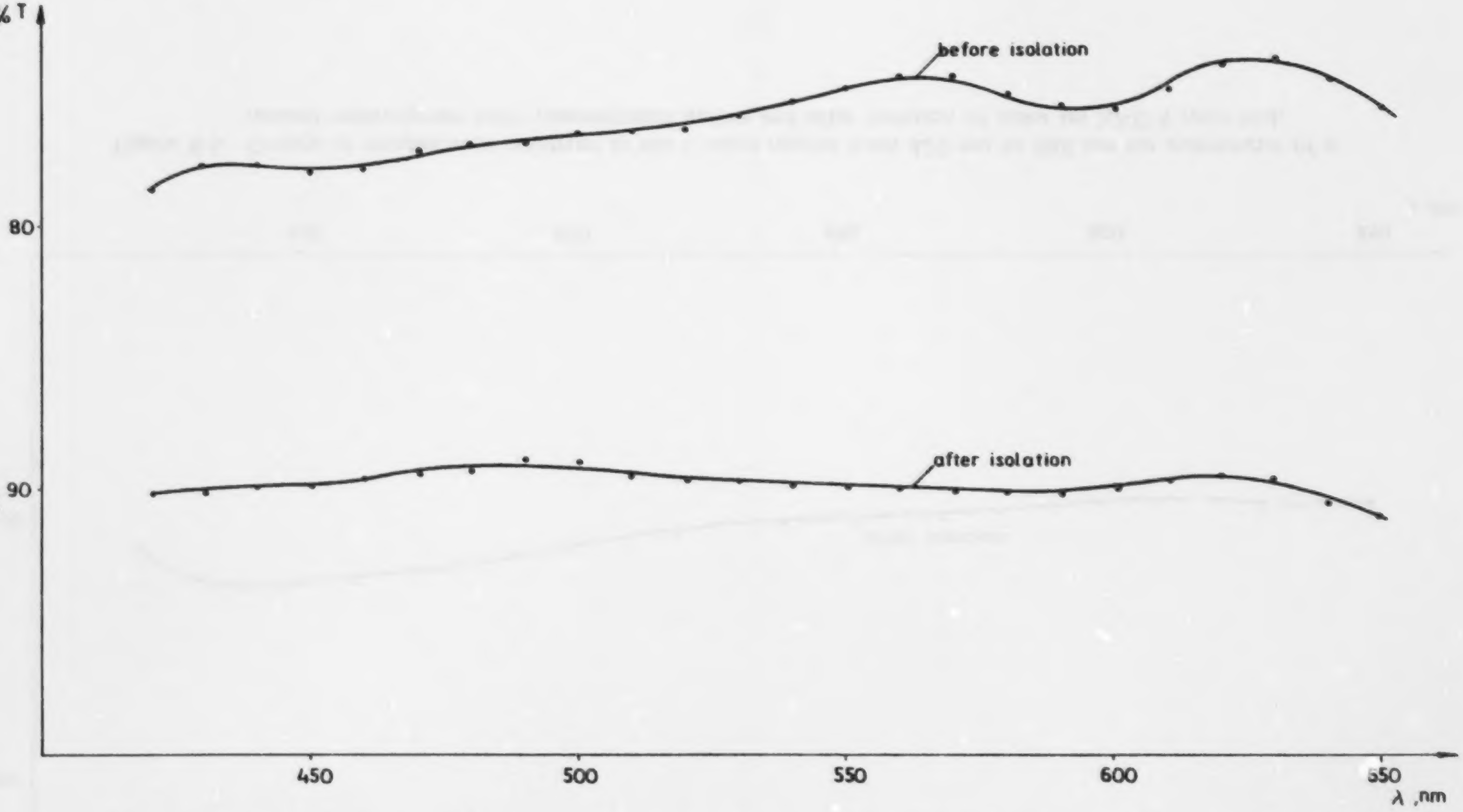


Figure 4-4. Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for wastewater of a characteristic blue-green color before and after isolation of color on XAD-4 resin bed.

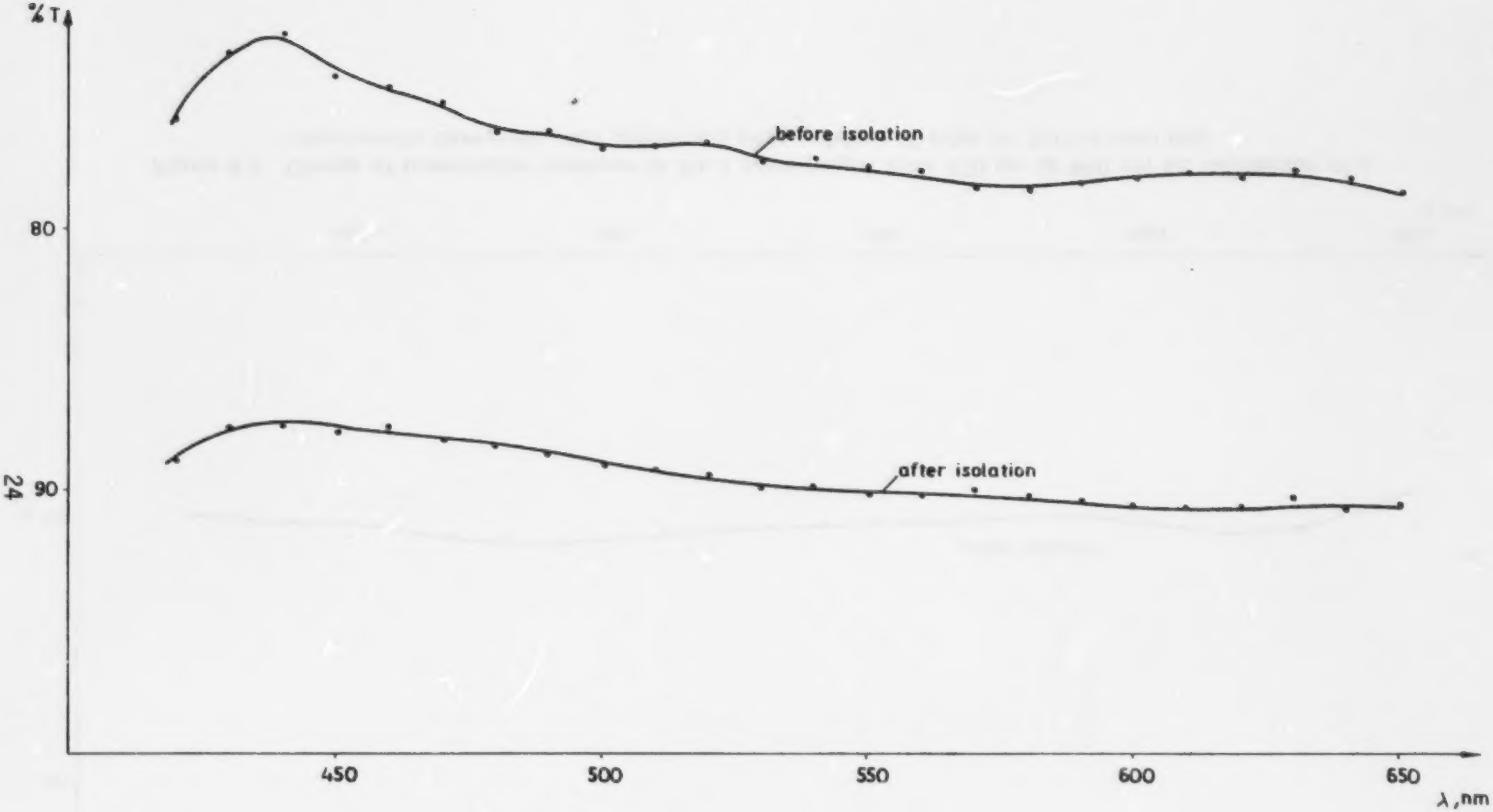


Figure 4-5. Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for wastewater of a natural yellow-green color concentrated before and after isolation of color on XAD-4 resin bed.

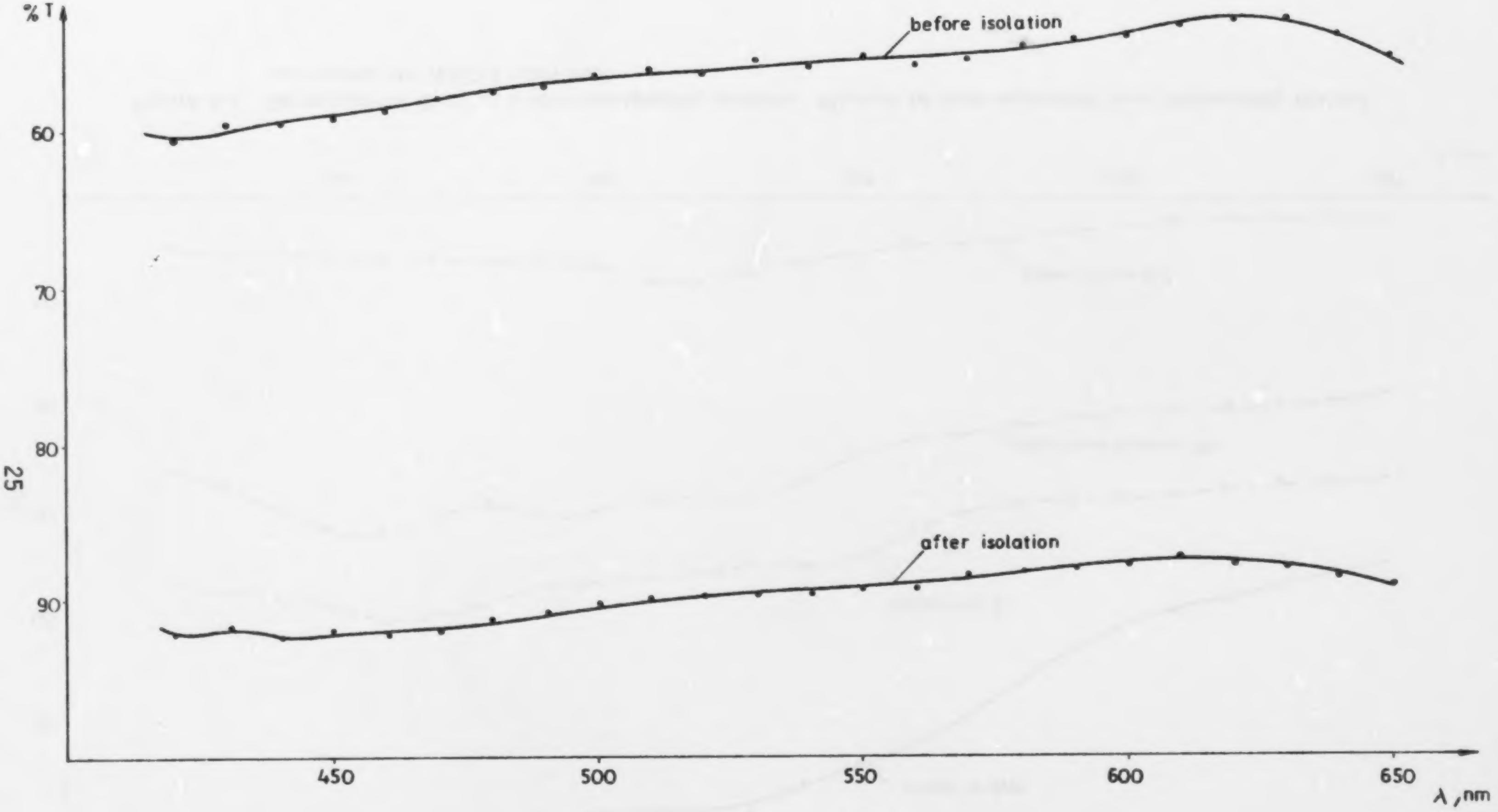


Figure 4-6. Change of transmission spectrum in the λ value ranged from 420 nm to 650 nm for wastewater of a characteristic blue-green color, concentrated before and after isolation of color on XAD-4 resin bed.

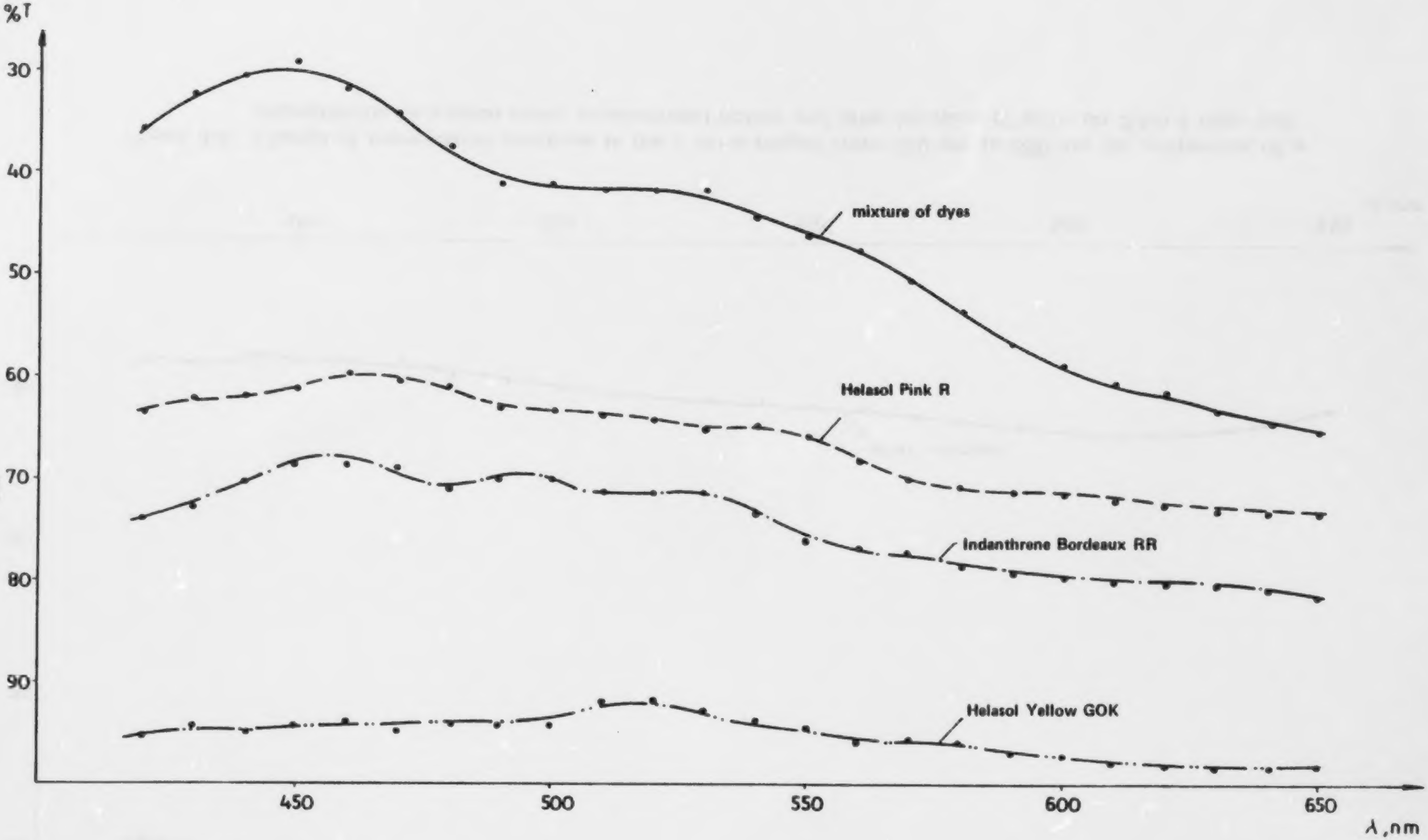


Figure 4-7. Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater on XAD-4 resin bed.

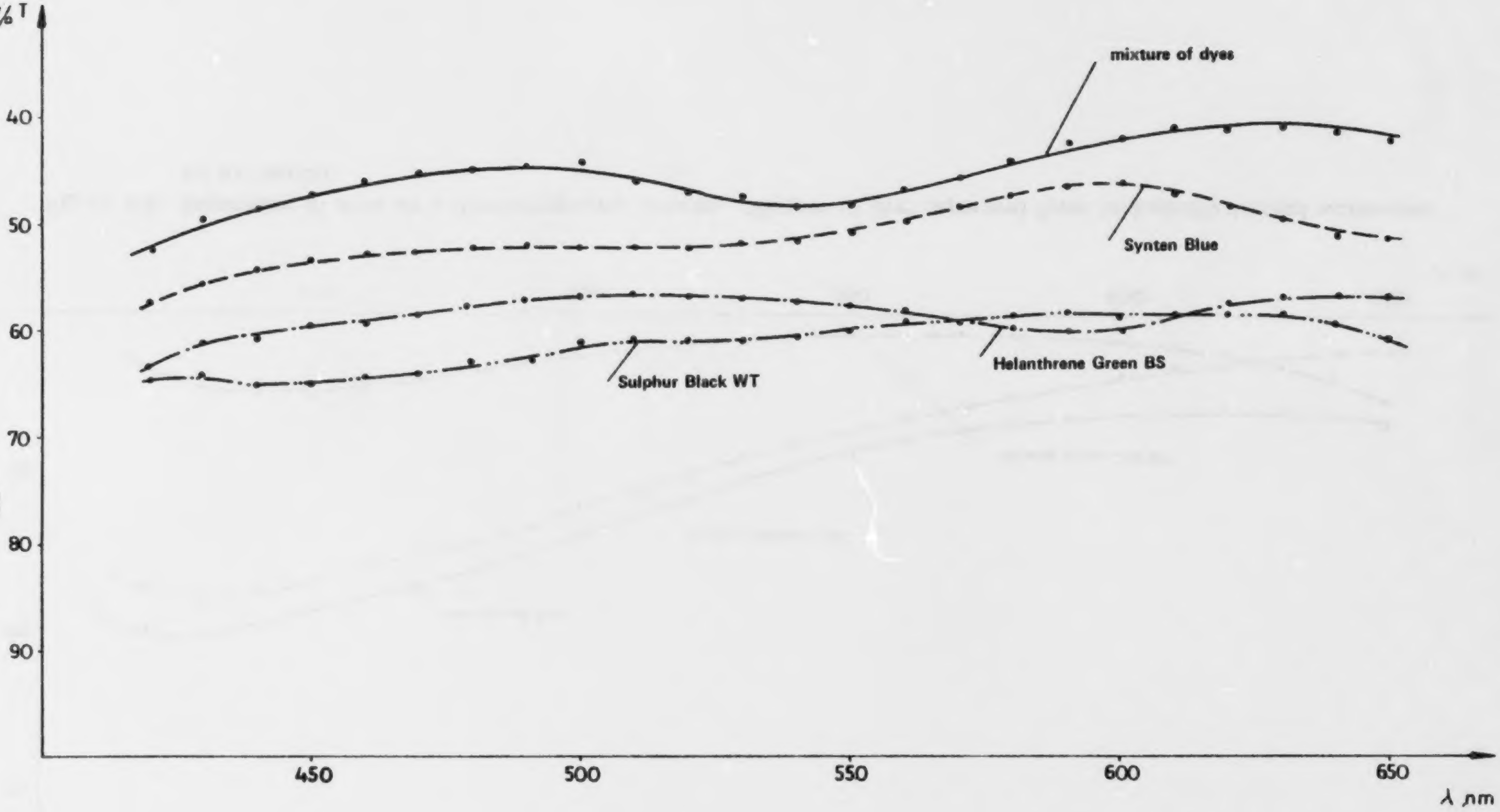


Figure 4-8. Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater on XAD-4 resin bed.

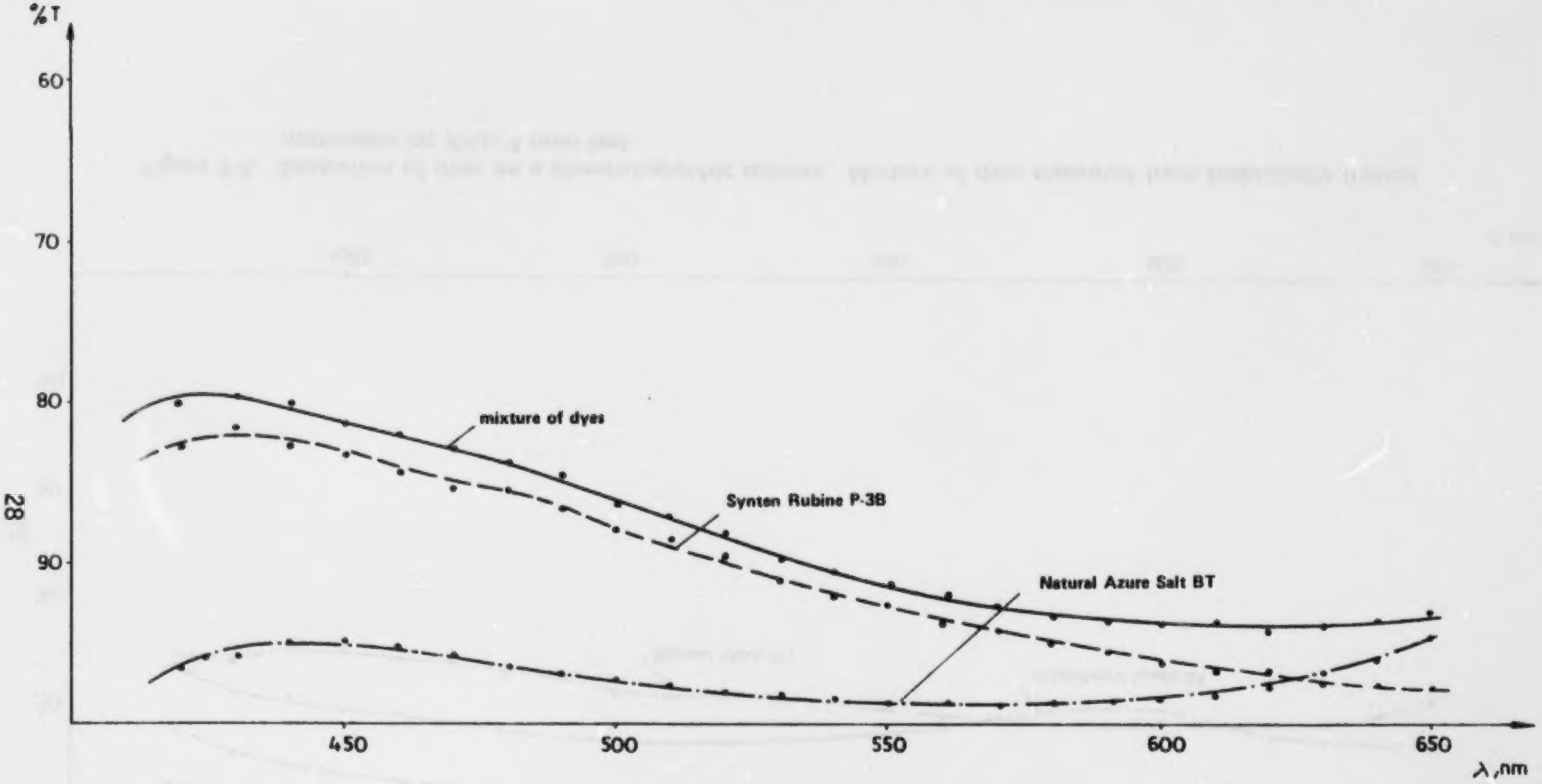


Figure 4-9. Separation of dyes on a chromatographic column. Mixture of dyes separated from biologically treated wastewater by extraction.

Table 4-1. a. Values of relative extinction at 450 nm for 10 wastewater samples treated biologically

n	x_i	$(x_i - \bar{x})$	$(x_i - x)^2$
1	0.58	0.08	0.0064
2	0.56	0.06	0.0036
3	0.50	0.00	0
4	0.46	0.04	0.0016
5	0.40	0.10	0.0100
6	0.40	0.10	0.0100
7	0.49	0.01	0.0001
8	0.54	0.04	0.0016
9	0.55	0.05	0.0025
10	0.54	0.04	0.0016
Sum	5.02		0.0374

b. Values of relative extinction at 500 nm for 10 wastewater samples treated biologically

n	x_i	$(x_i - \bar{x})$	$(x_i - x)^2$
1	0.40	0.02	0.0004
2	0.41	0.03	0.0009
3	0.40	0.02	0.0004
4	0.30	0.10	0.0100
5	0.30	0.10	0.0100
6	0.42	0.04	0.0016
7	0.43	0.05	0.0025
8	0.40	0.02	0.0004
9	0.40	0.02	0.0004
10	0.30	0.01	0.0001
Sum	3.76		0.0267

Table 4-2. a. Values of relative extinction at 450 nm for 10 wastewater samples treated by means of coagulation

n	x_i	$(x_i - \bar{x})$	$(x_i - x)^2$
1	0.50	0.00	0
2	0.50	0	0
3	0.43	0.07	0.0049
4	0.40	0.10	0.0100
5	0.56	0.06	0.0036
6	0.40	0.10	0.0100
7	0.56	0.06	0.0036
8	0.50	0	0
9	0.58	0.08	0.0064
10	0.56	0.06	0.0036
Sum	4.99		0.0421

b. Values of relative extinction at 500 nm for 10 wastewater samples treated by coagulation

n	x_i	$(x_i - \bar{x})$	$(x_i - x)^2$
1	0.40	0.04	0.0016
2	0.40	0.04	0.0016
3	0.30	0.06	0.0036
4	0.30	0.06	0.0036
5	0.44	0.08	0.0064
6	0.32	0.04	0.0026
7	0.36	0	0
8	0.41	0.05	0.0025
9	0.30	0.06	0.0036
10	0.38	0.02	0.0004
Sum	3.61		0.0249

Table 4-3. Dye recovery on column with resin XAD-4 and percentage of dye retention on chromatographic column

Dye group	Name of dye	Initial solution	Dye concentration in initial solution, mg/l	Dye recovery from solutions on column resin XAD-4		Analysis of column chromatography		Combined percentage of recovery
				%	mg/l	%	mg/l	
Sulfuric	Sulphur Black WT	1. Water	5	12.5	0.625	28.5	0.179	3.5
		2. Wastewater after biolog. treatment	5	10.5	0.525	33.6	0.176	3.52
	Sulphur Khaki G	1. Water	5	25.0	1.25	20.6	0.257	5.1
		2. Wastewater after biolog. treatment	5	22.5	1.12	15.4	0.172	3.4
		3. Wastewater from dyeworks	40,000	29.2	11,680	40.3	4,674.8	11.6
Glacial	Natural Azure Salt BT	1. Water	5	70	3.50	82.0	2.87	57.4
		2. Wastewater after biolog. treatment	5	86.1	4.30	75.6	3.24	65.1
		3. Wastewater from dyeworks	5,000	81.1	4,055	73.5	2,976	59.5
Vat	Helanthrene Green BS	1. Water	5	18.8	0.940	44.4	0.410	8.34
		2. Wastewater after biolog. treatment	5	17.7	0.885	32.5	0.287	5.75
		3. Wastewater from dyeworks	15,000	36.6	5,490	55.5	3,046	20.3
	Helanthrene Olive BT	1. Water	5	24.6	1.230	45.5	0.559	11.2
		2. Wastewater after biolog. treatment	5	29.5	1.475	40.1	0.591	11.8
		3. Wastewater from dyeworks	10,000	45.5	4,550	86.6	3,940	39.4

Table 4-3 (con.)

Dye group	Name of dye	Initial solution	Dye concentration in initial solution, mg/l	Dye recovery from solutions on column resin XAD-4		Analysis of column chromatography		Combined percentage of recovery
				%	mg/l	%	mg/l	
Indigosol	Helasol Yellow GOK	1. Water	5	90.5	4.52	95.2	4.30	86.1
		2. Wastewater after biolog. treatment	5	90.8	4.54	96.0	4.35	27.1
		3. Wastewater from dye-works	35,000	85.6	29,960	75.0	22,470	64.2
	Helasol Grey BL	1. Water	5	83.5	4.17	55.4	2.31	46.2
		2. Wastewater after biolog. treatment	5	88.4	4.42	50.4	2.22	44.5
	Helasol Orange RK	I. Water	5	70.0	3.5	60.3	2.11	42.2
		2. Wastewater after biolog. treatment	5	74.1	3.7	55.3	2.04	40.9
	Helasol Pink R	1. Water	5	60.3	3.01	56.1	1.68	33.8
		2. Wastewater after biolog. treatment	5	64.4	3.22	40.4	1.30	26.0
		3. Wastewater from dye-works	25,000	91.2	22,940	81.6	18,727	74.2
Reactive	Helaktyn Yellow DGR	1. Water	5	94.6	4.73	76.5	3.61	72.3
		2. Wastewater after biolog. treatment	5	95.7	4.78	70.5	3.36	67.4
		3. Wastewater from dye-works	30,000	98.2	29,460	58.2	17,145	57.0
	Drimarene Green X-2BL	1. Water	5	91.5	4.57	90.2	4.12	82.5
		2. Wastewater after biolog. treatment	5	91.8	4.59	85.6	3.92	78.5

Table 4-3 (con.)

Dye group	Name of dye	Initial solution	Dye concentration in initial solution, mg/l	Dye recovery from solutions on solumn resin XAD-4		Analysis of column chromatography		Combined percentage of recovery
				%	mg/l	%	mg/l	
Reactive (con.)	Remazol Brilliant Blue	1. Water	5	95.2	4.76	82.6	3.93	78.6
		2. Wastewater after biolog. treatment	5	95.5	4.77	75.2		
	Helaktyn Black F-5B	1. Water	5	71.5	3.57	65.6	3.58	46.9
		2. Wastewater after biolog. treatment	5	74.1	3.70	60.2	2.22	44.6
		3. Wastewater from dyeworks	25,000	85.4	21,350	65.0	13,877	55.5

Table 4-4. Dye recovery on column with resin XAD-4 and percentage of dye retention on the chromatographic column

	Composition mixtures	Process	Initial dye concentration	Color recovery of mixtures on column with resin XAD-4, %	Analysis of column chromatography combined % of recovery of individual dyes
I	Natural Azure Salt BT	1. before ozonation	50	60.5	76.5
	Helanthrene Green BS	1a. before ozonation	50		32.5
	Natural Azure Salt BT	2. before ozonation	50	40.1	56.1
	Helanthrene Green BS	2a. before ozonation	50		28.0
II	Base of Scarlet	1. before ozonation	50		52.5
	Natural Azure Salt BT	1a. before ozonation	50	40.1	82.6
	Sulphur Black WT	1b. before ozonation	50		26.5
	Base of Scarlet	2. after ozonation	50		50.0
	Natural Azure Salt BT	2a. after ozonation	50	36.2	60.2
	Sulphur Black WT	2b. after ozonation	50		15.4
III	Helasol Green	1. before ozonation	50		44.4
	Indanthren Bordeaux RR	1a. before ozonation	50	50.5	54.8
	Helaktyn Yellow	1b. before ozonation	50		60.3
	Helasol Green	2. after ozonation	50		24.5
	Indanthren Bordeaux RR	2a. after ozonation	50	44.5	40.1
	Helaktyn Yellow	2b. after ozonation	50		55.0
IV	Synten Azure	1. before ozonation	50		26.5
	Helasol Yellow GOK	1a. before ozonation	50	65.0	95.0
	Drimarene Green X-2BL	1b. before ozonation	50		85.0
	Synten Azure	2. after ozonation	50		24.0
	Helasol Yellow GOK	2a. after ozonation	50	50.6	70.5
	Drimarene Green X-2BL	2b. after ozonation	50		75.2
V	Helaktyn Yellow D5GN	1. before ozonation	50	20.0	46.0
	Helasol Grey BL	1a. before ozonation	50		20.0
	Helaktyn Yellow D5GN	2. after ozonation	50	17.1	25.2
	Helasol Grey BL	2a. after ozonation	50		14.0

Table 4-5. Removal of dyes from wastewater by extraction

Type of dye	Name of dye*	% of individual dye extracted from colored wastewater	% change measured spectrophotometrically
Sulfuric	Sulphuric Khaki G	15.0	-
Glacial	Natural Azure Salt BT	59.3	-
Vat	Helanthrene Green BS	10.9	-
Indigosol	Helasol Yellow GOK	66.0	-
	Helasol Orange RK	62.8	-
Reactive	Helaktyn Yellow DGR	77.5	-
	Drimarene Green X-2BL	79.6	-
Dispersed	Synten Rubine P-38	44.3	-
	Synten Azure	15.6	-
Natural yellow-green wastewater		-	15.6
Wastewater with a specific blue coloring		-	30.2

*See pages 12 and 13 for Colour Index information on dyes in this table.

Table 4-6. Eluting solvents for various groups of dyes

Mixtures of dyes*	Eluting solvent
Indanthren Bordeaux RR Helasol Yellow GOK Helasol Pink R	Ethyl alcohol
Sulphur Black WT Syntene Azure Helanthrene Green BS	Chloroform
Natural Azure Salt BT Drimarene Green X-2BL	Ethyl Octane: n-propanol (1:1)
Helanthrene Olive BS Helaktyn Red F5B Helaktyn Yellow DGR	Methanol:petroleum ether (2:1)
Synten Rubine P-3B Sulphur Khaki G Natural Azure Salt BT	Ethyl Octane: n-propanol: n-butanol: (2:1:3)
Remazol Brilliant Blue Helasol Grey BL Helasol Orange RK	Chloroform:acetone: isopropanol (3:4:2)
Indanthren Bordeaux RR Synten Navy Blue Drimarene Green X-2BL	Ethyl alcohol:n-butanol (2:1)

*See pages 12 and 13 for _Colour Index_ information on dyes in this table.

Table 4-7. Column chromatography for dye mixtures in water and wastewater solution

Dye mixture in water and wastewater solution*	Eluting solvent	Chromatographic column filling
Indanthren Bordeaux RR	Petroleum ether (1:1)	Silica gel
Helasol Yellow GOK		Aluminum oxide
Helasol Pink R		Calcium carbonate
Sulphur Black WT	Ethyl octane	Magnesium oxide
Synten Azure		Siliceous gel
Helanthrene Green BS		Calcium carbonate
Natural Azure Salt BT	Butanol: chloroform (1:1)	Silica gel
Drimarene Green X-2BL		Silica gel
Helanthrene Olive BS	Methanol petroleum ether	Aluminum oxide
Helaktyn Black F5B		Silica gel
Helaktyn Yellow DGR		Silica gel
Synten Rubine P-3B	Chloroform	Silica gel
Sulphur Khaki G		Magnesium oxide
Natural Azure Salt BT		Silica gel
Indanthren Bordeaux RR	Butanol:n-propanol (2:1)	Silica gel
Synten Navy Blue		Silica gel
Drimarene Green X-2BL		Silica gel

*See pages 12 and 13 for Colour Index information on dyes in this table.

Table 4-8. Column chromatography for dye mixtures in Table 4-4

Mixture with composition given in table 4-4	Eluting solvent
I before ozonation I after ozonation	Butanol:chloroform (1:1)
II before ozonation II after ozonation	Ethyl octane
III before ozonation III after ozonation	Butanol:n-propanol (2:1)
IV before ozonation IV after ozonation	Ethyl octane
V before ozonation V after ozonation	Methanol:petroleum ether (1:1)

Table 4-9. Column chromatography for dye mixtures from dyehouse

Mixture of dyes from dyehouse*	Eluting solvent	Column filling
Helanthrene Green BS Helanktyn Red F5B	Ethyl octane	Silica gel
Helasol Yellow GOK Synten Rubine P-3B	Petroleum ether + petrol (8:1)	Aluminium oxide
Natural Azure Salt BT Helasol Pink R	Butanol: Chloroform (1:1)	Calcium carbonate
Synten Azure Sulphur Khaki G	Chloroform	Silica gel
Helanthrene Olive BT Helaktyn Yellow D5GN	Methanol: petroleum ether (1:1)	Magnesium oxide

*See pages 12 and 13 for Colour Index information on dyes in this table.

Table 4-10. Percent dye recovery from wastewater colored with various dye mixtures

Dye mixture*	Developing solvent	% of dye recovery
Helanthrene Green BS	Chloroform	15.3
Helaktyn Red F5B		18.0
Helasol Yellow GOK	Ethyl Alcohol	25.5
Synten Rubine P-3B		30.0
Natural Azure Salt BT	Ethyl octane: n-propanol: n-butanol: (2:1:3)	10.0
Helasol Pink R		12.0
Synten Azure	Ethyl alcohol: n-butanol (2:1)	5.0
Sulphur Khaki G		15.0
Helanthrene Olive BT	Methanol	35.0
Helaktyn Yellow D5-GN		45.0

*See pages 12 and 13 for Colour Index information on dyes in this table.

Table 4-11. Percent recovery from dyes isolated by extraction

Kind of dye*	% dye recovery
Sulphur Khaki G	15.2
Drimarene Green X-2BL	10.0
Natural Azure Salt BT	7.5
Synten Rubine P-3B	13.6
Helasol Yellow GOK	17.0
Helanthrene Green BS	12.4

*See pages 12 and 13 for Colour Index information on the dyes in this table.

SECTION 5

CHARACTERISTICS OF TEXTILE PROCESSES AND PILOT PLANT OPERATION

DESCRIPTION OF THE ANDRYCHOW COTTON PLANT AND ITS PRODUCTION

The Andrychow Cotton Plant (ACP) is engaged in the production of bedclothes, clothing, and tent fabrics from cottons and synthetics. The fabrics produced are mainly a mixture of cotton and synthetic fibers, but some are pure cotton. The production of raw materials at ACP during the last few years has been 30 percent synthetics and 70 percent cotton.

The size of ACP production in the period of research was about 55,000,000 m --about 9,000,000 kg--of fabric per year. ACP uses about 7,800 m^3/d of water for technological and other purposes; of this, about 6,000 m^3/d is discharged in the form of wastewater. Different kinds of chemical agents and dyes are used in the production of fabrics. The average yearly consumption of individual chemicals is set out in table 5-1.

The plant has five production departments: the spinning mill, the weaving mill, the yarn-dyeing department, finishing plant A, and finishing plant B.

Because process wastewater is not discharged from the spinning and weaving mills, these departments will not be discussed in the present report.

The fiber-dyeing department is a transitional department between the spinning mill and the weaving mill. Yarn for ready-colored fabrics is bleached and dyed here before undergoing the weaving process. The fiber-dyeing department produces about 12 percent of the total weight of fabrics produced at ACP, but the technological wastewater from the fiber-dyeing department is about 17 percent of the total amount of wastewater discharged by ACP. Fiber treatment consists of dyeing and bleaching. Indigosol, vat, sulfuric, and reactive dyes are used for the dyeing of pure cotton yarn; cottestrense and dispersed-vat dyes are used for the dyeing of yarn that blends synthetic and cotton fibers.

In finishing plants A and B the fabrics are subjected to final treatment. The production processes in the two finishing plants are roughly identical. Differences lie mainly in the different machines with which the plants are equipped. Both the size of production and the amount of wastewater discharged are approximately equal for the two finishing plants

(2,500 m^3/d each). The schematic plan of finishing plant A is given in figure 5-1, and that for finishing plant B is given in figure 5-2.

Finishing plants A and B are equipped with modern machines for dyeing, bleaching, singeing, and mercerization. These processes take place with a continuous movement of fabrics through the particular machines. As a rule, the machines are multicompartmental. The fabric running through individual compartments is subjected to successive processing operations. The operating scheme for each type of dye used in the PAD-STEAM continuous dyeing machine is given in figures 5-3 and 5-4. Unlike plant A, plant B uses larger quantities of dyes and employs a PAD-STEAM continuous dyeing machine that is one washing compartment shorter than the machine used in Plant A.

The operating schemes of the washing, bleaching, and mercerization processes for both finishing plants are given in figures 5-5 and 5-6. Finishing plant A is equipped with a modern Benninger bleaching and washing machine and modern machines for mercerization and singeing. The machines of the bleaching house in finishing plant B are older types. Movable reaction tanks are also used in plant B. Some fabrics undergo treatment in these before the bleaching or washing process.

Since the ACP is generally a modern factory, and its wastewater is representative for this type of industry in Poland, the results of the research conducted there apply to most modern textile plants.

SCOPE OR RESEARCH WORK CARRIED OUT AT THE EXPERIMENTAL PILOT PLANT IN ANDRYCHOW

Municipal sewage from the town of about 13,000 inhabitants and textile wastewater from the ACP flows to the combined municipal and industrial wastewater treatment plant in Andrychow. Other minor industries discharging pretreated wastewater to the treatment plant are a machinery factory and a slaughterhouse. The total amount of waste according to the last assessment in 1976 is on the average 12,000 m^3/d. The proportion of textile to municipal wastewater is approximately 1:1. At the municipal treatment plant the wastewater undergoes mechanical treatment according to the plan presented in figure 5-7. A part of the wastewater mixed after mechanical treatment was collected for further treatment at the pilot plant.

The experimental pilot plant consisted of a biological treatment unit with activated sludge aerated with compressed air, and a building in which the tertiary treatment plant was installed. The pilot biological plant was set into operation in 1973. In the period of early operation during the second half of 1973, it operated with:

- a 1:1 proportion of municipal and textile wastewater,
- a wastewater supply rate of 2.67 m^3/h,
- a 6-h aeration time with activated sludge,
- 2,000 to 5,000 mg/l of mixed-liquor suspended solids in the aeration tank, and
- a sludge volume index of 53.5 to 240.3 mg/l.

These parameters were maintained until October 10, 1975, when the proportion of textile to municipal wastewater was changed to 2:1 to increase the concentration of the mixed wastewater. The characteristics of the pilot activated sludge process operation during the first period are indicated in table 5-2.

After the change in wastewater proportions, the pollutant concentrations supplied to the pilot biological treatment plant increased. At the same time, the treatment plant's effectiveness decreased (table 5-3) while the same operating parameters were maintained for the activated sludge process. Biologically treated wastewater was fed to the pilot tertiary treatment plant in accordance with a set timetable. The model treatment units were assembled from Plexiglas columns 0.12 to 0.15 m in diameter and differing in height depending on the process requirements.

First of all, investigations of the filtration and adsorption processes were carried out during the period from February 12, 1974, to August 30, 1975. The pilot plant for study of these processes was constructed according to the scheme in figure 5-8. The adsorption process was carried out in a one-, two-, or three-stage system, and also in a parallel system when different operating conditions of the adsorption process were evaluated. Before reaching the adsorption plant, the wastewater always passed through a filtration column, on which observations were made of the filtration effects with different filter media. Separate investigations of the filtration process were carried out on four additional filtration columns working in parallel, but with different parameters. Investigations of both processes were conducted in columns 0.15 m in diameter and 2 m high.

The coagulation process was carried out at the pilot plant in two different systems: conventional coagulation in a suspended floc reactor, and upflow contact coagulation. The conventional coagulation process was carried out in a clarifier with vertical flow, with a layer of suspended flocs, working together with an anthracite-sand filter (figure 5-9.) The clarifier was 0.3 m in diameter and 4 m high. Investigations were carried out in two series: the first from June to November 1975, and the second from May to June 1976. Introductory investigations of upflow contact coagulation on different filter beds were conducted on two columns 0.15 m in diameter and 3.0 m high, from February to May 1975 (figure 5-10). From June to November 1975, the contact coagulation process was carried out on two columns with identical beds, for one of which preliminary pH control and oxidation with sodium hypochlorite was carried out. In August 1976, supplementary investigations of contact coagulation with pH control and oxidation with sodium hypochlorite were conducted. In this series a filtration column with an anthracite-sand bed was also installed after the coagulation column.

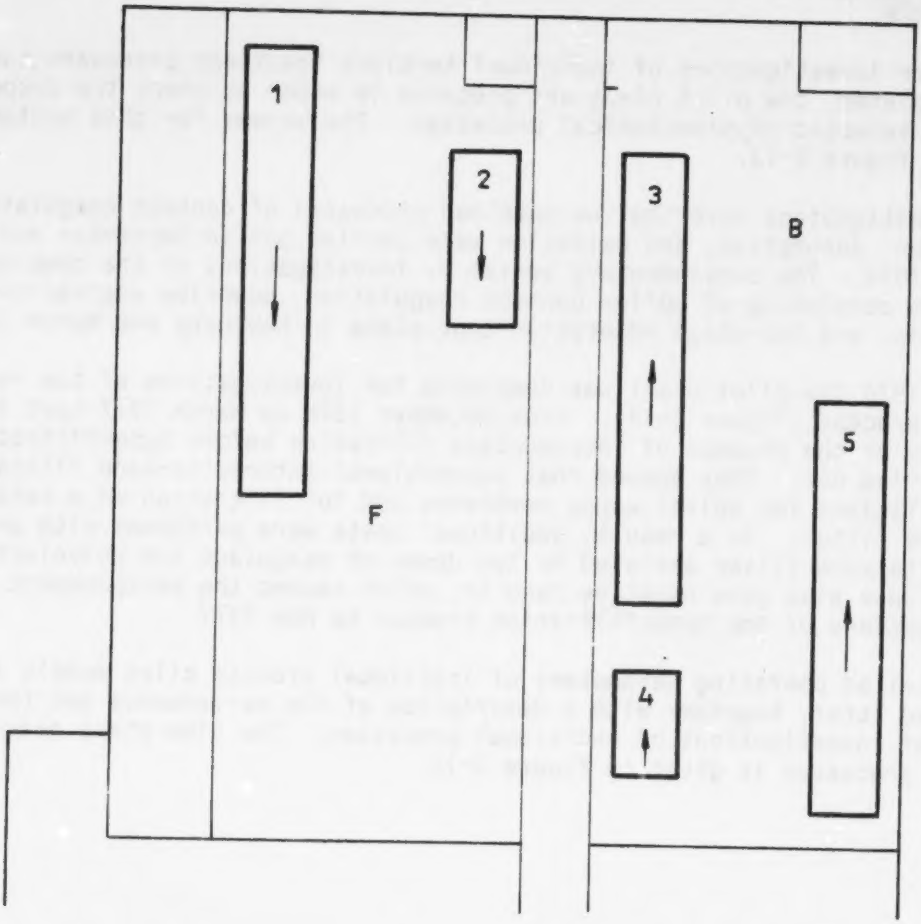
Pilot investigations of the ion-exchange process were carried out from September 1975 to February 1976. The scheme of the pilot plant for the study of this process is given in figure 5-11. Plexiglas columns 0.12 m in diameter and 2.1 m high were used to construct the plant. Investigations of the ozone-oxidation process were conducted in reactors formed by columns 0.12 m in diameter and 2.1 m high (figure 5-12), filled with ceramic pieces to increase the efficiency of the reaction of wastewater and ozone. The pilot investigation of the oxidation process was carried out from May to August 1976.

After investigations of individual tertiary treatment processes had been completed, the pilot plant was prepared in order to check the cooperation of selected physicochemical processes. The scheme for this system is given in figure 5-13.

Investigations covering the combined processes of contact coagulation, filtration, adsorption, and oxidation were carried out in September and October 1976. The supplementary series of investigations of the combined processes consisting of upflow contact coagulation, downflow anthracite-sand filtration, and two-stage adsorption took place in February and March 1977.

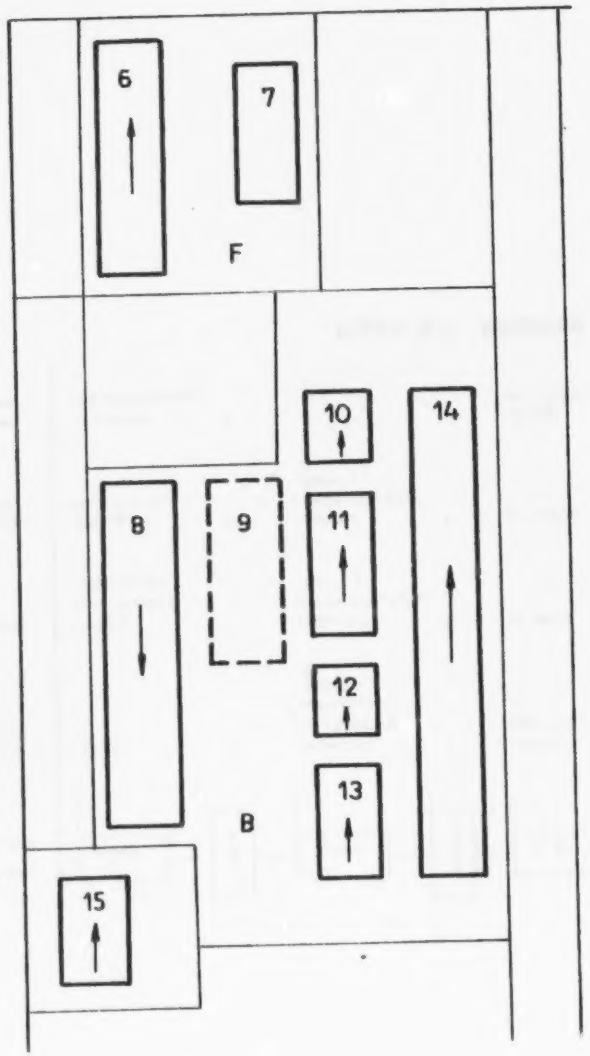
In 1976 the pilot plant was completed for investigations of the reverse osmosis process (figure 5-14). From December 1976 to March 1977 test investigations of the process of introductory filtration before hyperfiltration were carried out. They showed that conventional anthracite-sand filtration is insufficient for spiral wound membranes and for filtration on a ceramic micropore filter. As a result, additional tests were performed with an anthracite-sand filter assisted by low doses of coagulant and polyelectrolyte. These also gave negative results, which caused the postponement of investigations of the hyperfiltration process to May 1977.

Detailed operating parameters of individual process pilot models are discussed later, together with a description of the performance and the result of investigations of individual processes. The time-phase diagram for all processes is given in figure 5-15.



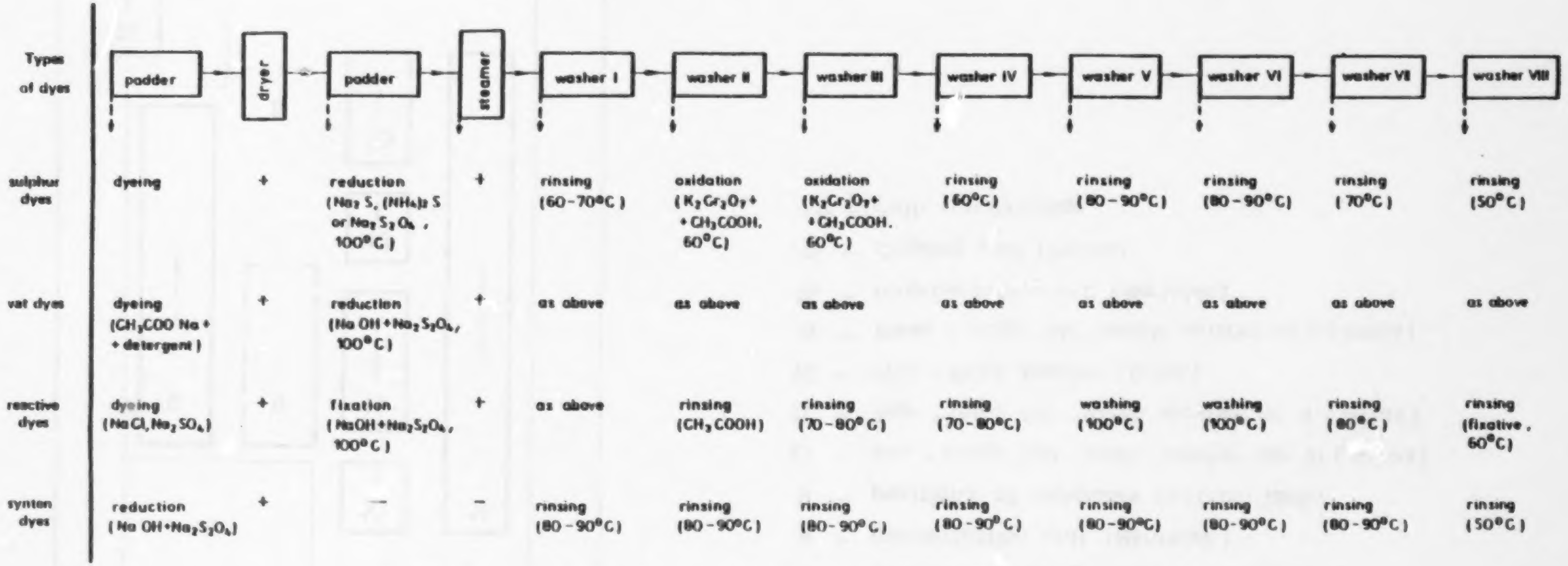
F – dye house
B – bleach house
1 – PAD – STEAM continuous dyeing machine
2 – THERMOSOL continuous dyeing machine
3 – bleaching unit type Formula Go (Benninger)
4 – singeing unit (Benninger – Osthoff)
5 – mercerization unit (Benninger)
→ – cloth run direction

Figure 5-1. Finishing Plant A. Schematic plan of the bleach and dye houses.



F – dye house
B – bleach house
6 – continuous dyeing machine PAD - STEAM
7 – continuous dyeing machine THERMOSOL
8 – mercerization unit (Benteler)
9 – positions of moveable reaction tanks
10 – two - stage full - width washer no. III (Artos)
11 – four - stage full - width washer no. II (Artos)
12 – PAD – ROLL padder (Artos)
13 – three - stage full - width washer no. I (Artos)
14 – roap bleaching unit (Benteler)
15 – singeing unit (Parex)
→ – cloth run direction

Figure 5-2. Finishing Plant B. Schematic plan of the bleach and dye houses.



Types of dyes	padder	dryer	padder	steamer	washer I	washer II	washer III	washer IV	washer V	washer VI	washer VII	washer VIII
sulphur dyes	dyeing	+	reduction (Na_2S, $(NH_4)_2S$ or $Na_2S_2O_4$, 100°C)	+	rinsing (60–70°C)	oxidation ($K_2Cr_2O_7$ + CH_3COOH, 60°C)	oxidation ($K_2Cr_2O_7$ + CH_3COOH, 60°C)	rinsing (60°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (70°C)	rinsing (50°C)
vat dyes	dyeing (CH_3COONa + detergent)	+	reduction ($NaOH + Na_2S_2O_4$, 100°C)	+	as above	as above	as above	as above	as above	as above	as above	as above
reactive dyes	dyeing ($NaCl, Na_2SO_4$)	+	fixation ($NaOH + Na_2S_2O_4$, 100°C)	+	as above	rinsing (CH_3COOH)	rinsing (70–80°C)	rinsing (70–80°C)	washing (100°C)	washing (100°C)	rinsing (80°C)	rinsing (fixative, 60°C)
synton dyes	reduction ($NaOH + Na_2S_2O_4$)	+	—	–	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (50°C)

Figure 5-3. Finishing Plant A. Pad-steam dyeing machine processes.

Types of dyes	padder	dryer	padder	steamer	washer I	washer II	washer III	washer IV	washer V	washer VI	washer VII
indigosol dyes (dark shade)	dyeing ($NaNO_2$)	+	—	–	rinsing (H_2SO_4)	rinsing (20°C)	rinsing (Na_2CO_3)	washing	rinsing (80–90°C)	rinsing (80–90°C)	rinsing (50–60°C)
indigosol dyes (light shade)		–	dyeing ($NaNO_2$)	–	as above	as above	as above	as above	as above	as above	as above
sulphur dyes	dyeing	+	reduction (Na_2S, $(NH_4)_2S$ or $Na_2S_2O_4$, 100°C)	+	rinsing (60–70°C)	oxidation ($K_2Cr_2O_7$ + + CH_3COOH, 60°C)	oxidation ($K_2Cr_2O_7$ + + CH_3COOH, 60°C)	rinsing (80–90°C)	washing	as above	as above
vat dyes	dyeing (CH_3COONa + + detergent + + antifoaming agent)	+	reduction ($NaOH + Na_2S_2O_4$, 100°C)	+	as above	as above	as above	as above	as above	as above	as above
reactive dyes	dyeing ($NaCl + Na_2S_2O_4$)	+	fixation ($NaOH + Na_2S_2O_4$)	+	as above	washing	washing	as above	rinsing (80–90°C)	as above	as above
glacial dyes	padding (naphtoelane)	+	padding (naphtoelane base)	–	rinsing (30°C)	rinsing (80–90°C)	washing	washing	as above	as above	as above
cottestrense (type) mixed dyes	—	–	reduction ($NaOH + Na_2S_2O_4$)	+	as above	oxidation ($K_2Cr_2O_7$ + + CH_3COOH, 60°C)	oxidation ($K_2Cr_2O_7$ + + CH_3COOH, 60°C)	as above	washing	as above	as above
dispersed dyes	—	–	as above	+	as above	as above	as above	rinsing (80–90°C)	as above	as above	as above

Figure 5-4. Finishing Plant B. Pad-steam dyeing machine processes.

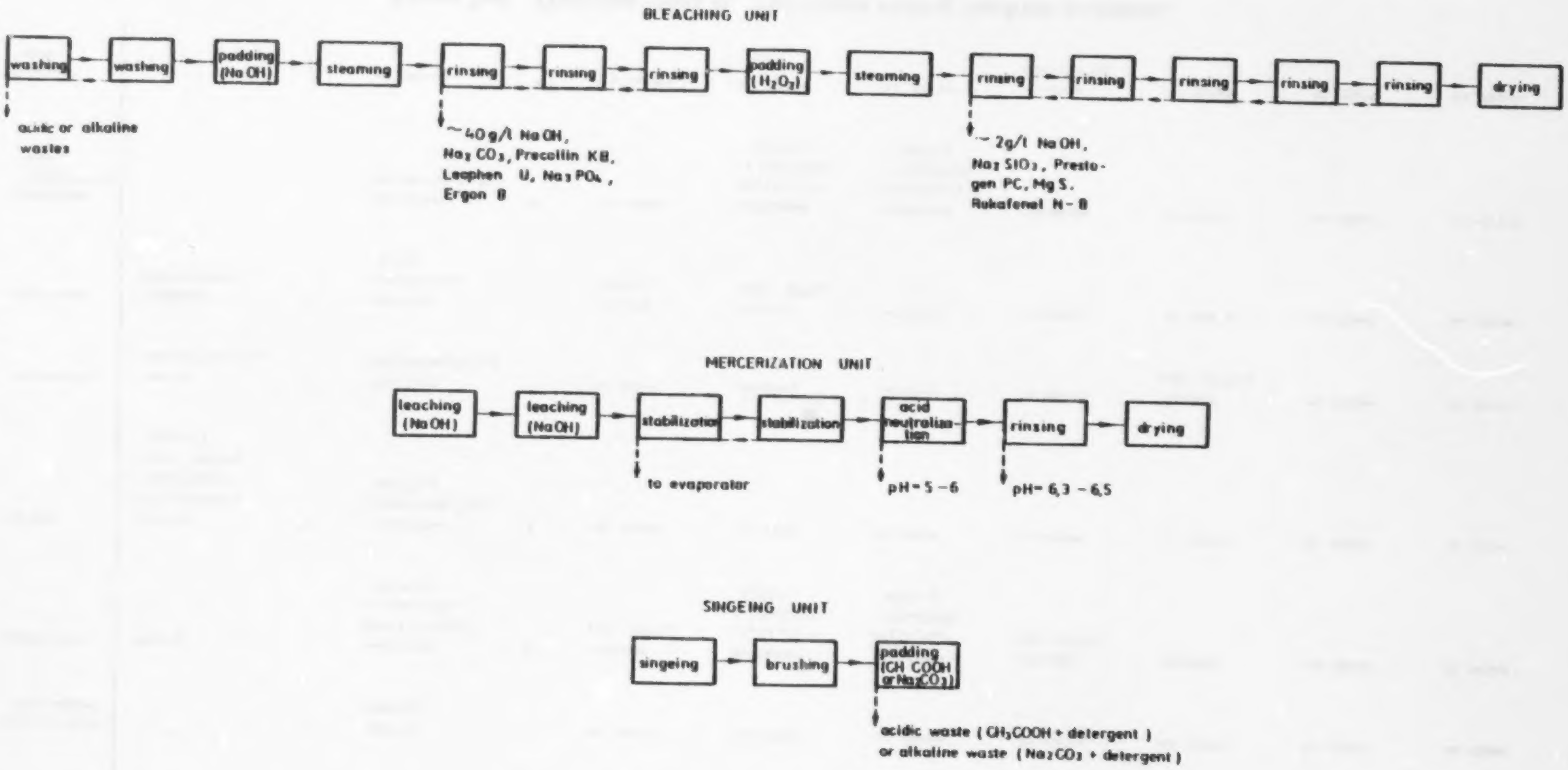

BLEACHING UNIT
washing
washing
padding (NaOH)
steaming
rinsing
rinsing
rinsing
padding (H_2O_2)
steaming
rinsing
rinsing
rinsing
rinsing
rinsing
drying
acidic or alkaline wastes
~40 g/l NaOH, Na_2CO_3, Precollin KB, Leophen U, Na_3PO_4, Ergon B
~2g/l NaOH, Na_2SiO_3, Prestogen PC, MgS, Rukafenal N-B
MERCERIZATION UNIT
leaching (NaOH)
leaching (NaOH)
stabilization
stabilization
acid neutralization
rinsing
drying
to evaporator
pH=5-6
pH=6,3-6,5
SINGEING UNIT
singeing
brushing
padding (CH_3COOH or Na_2CO_3)
acidic waste (CH_3COOH + detergent)
or alkaline waste (Na_2CO_3 + detergent)

Figure 5-5. Finishing Plant A. Bleach house.

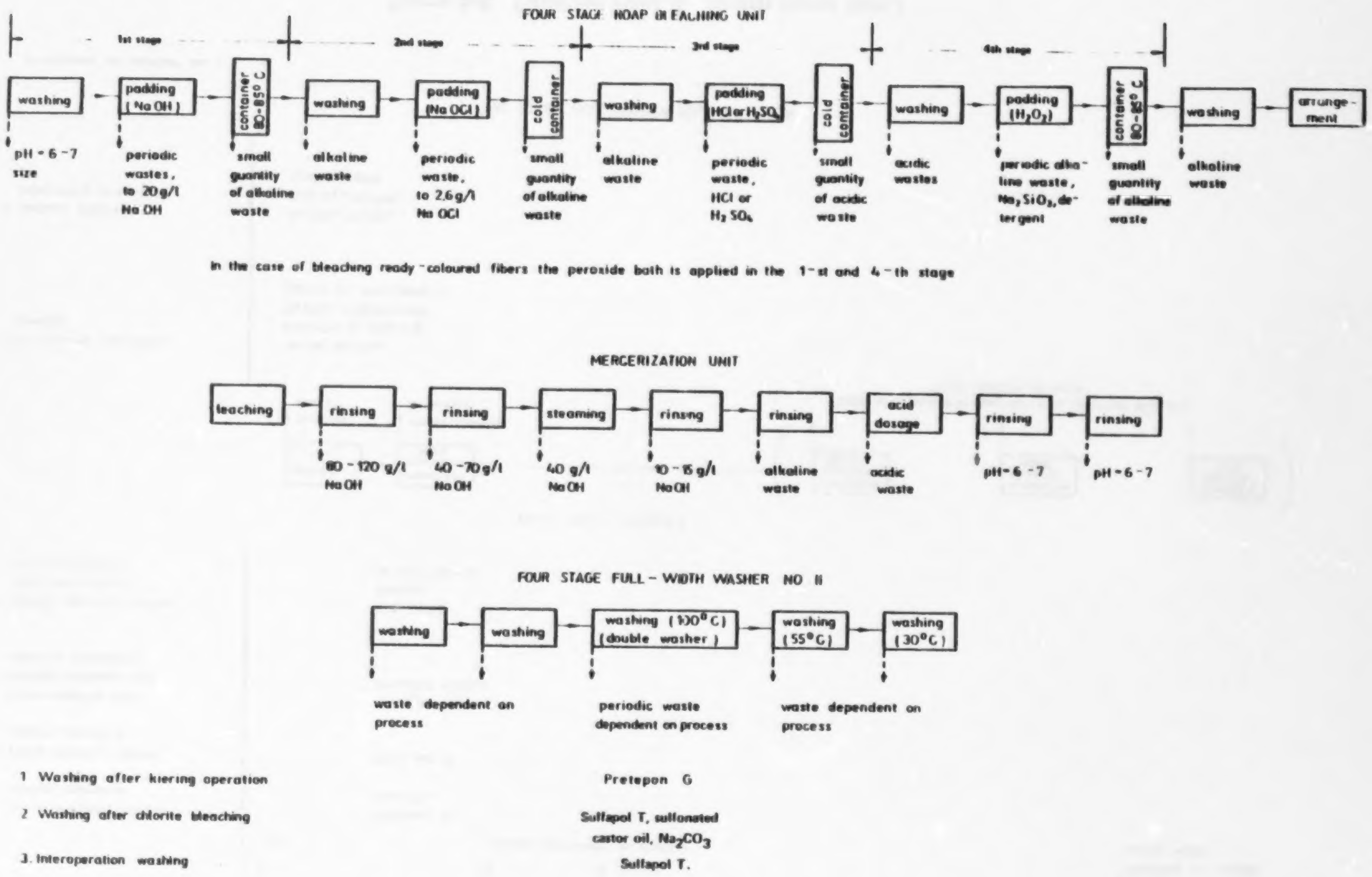

FOUR STAGE HOAP BLEACHING UNIT
1st stage
2nd stage
3rd stage
4th stage
washing
padding (Na OH)
container 80-85° C
washing
padding (Na OCl)
cold container
washing
padding HCl or H2SO4
cold container
washing
padding (H2O2)
container 80-85° C
washing
arrangement
pH = 6 - 7 size
periodic wastes, to 20 g/l Na OH
small quantity of alkaline waste
alkaline waste
periodic waste, to 2,6 g/l Na OCl
small quantity of alkaline waste
alkaline waste
periodic waste, HCl or H2 SO4
small quantity of acidic waste
acidic wastes
periodic alkaline waste, Na2 SiO3, detergent
small quantity of alkaline waste
alkaline waste
In the case of bleaching ready-coloured fibers the peroxide bath is applied in the 1-st and 4-th stage
MERCERIZATION UNIT
leaching
rinsing
rinsing
steaming
rinsing
rinsing
acid dosage
rinsing
rinsing
80 - 120 g/l Na OH
40 - 70 g/l Na OH
40 g/l Na OH
10 - 15 g/l Na OH
alkaline waste
acidic waste
pH = 6 - 7
pH = 6 - 7
FOUR STAGE FULL - WIDTH WASHER NO II
washing
washing
washing (100° C) (double washer)
washing (55° C)
washing (30° C)
waste dependent on process
periodic waste dependent on process
waste dependent on process
1 Washing after kiering operation
2 Washing after chlorite bleaching
3. Interoperation washing
Pretepon G
Sulfapol T, sulfonated castor oil, Na2CO3
Sulfapol T.

Figure 5-6. Finishing Plant B. Bleach house.

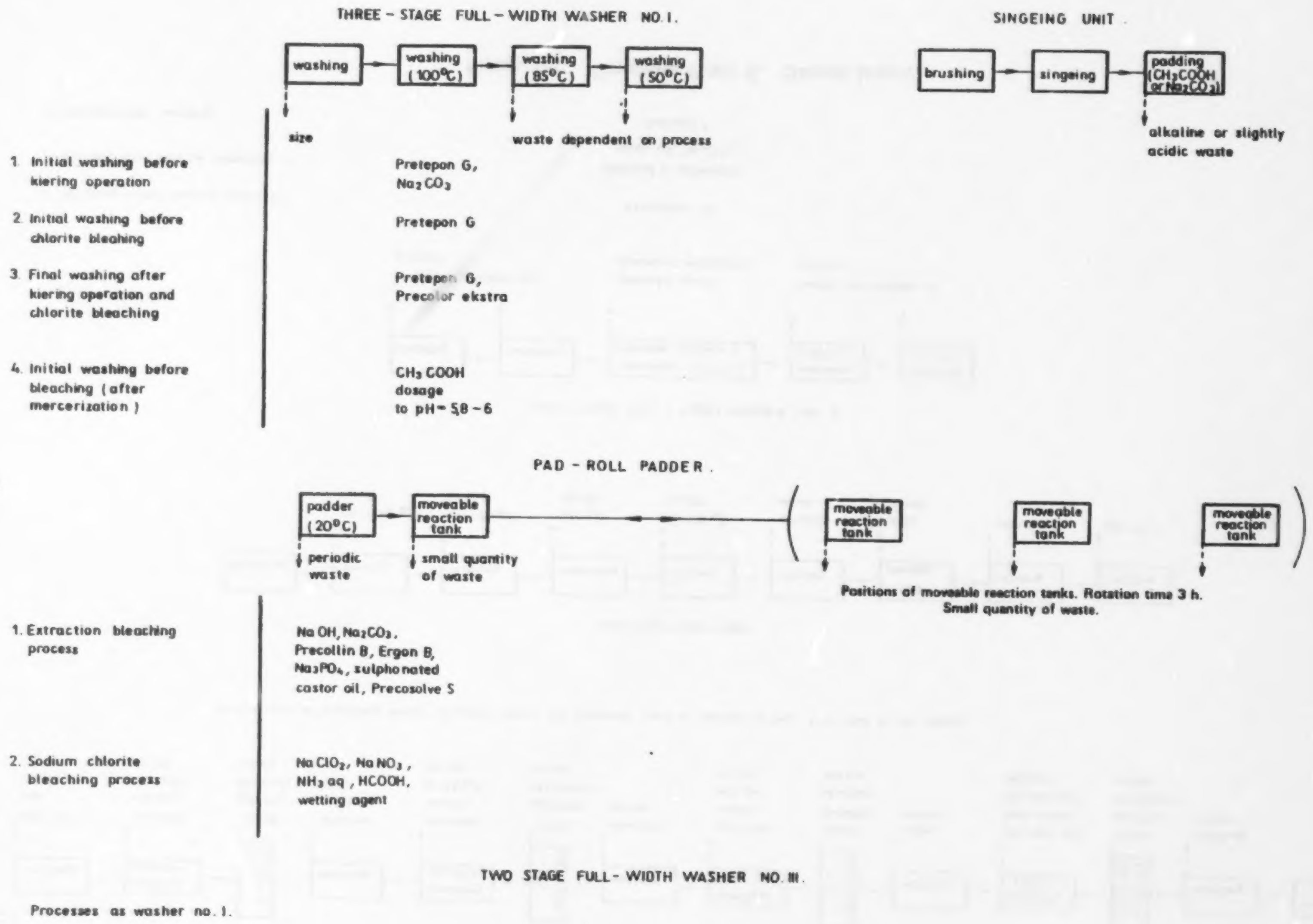

THREE - STAGE FULL - WIDTH WASHER NO. I.
washing
washing (100°C)
washing (85°C)
washing (50°C)
size
waste dependent on process
1. Initial washing before kiering operation
Pretepon G, Na₂CO₃
2. Initial washing before chlorite bleahing
Pretepon G
3. Final washing after kiering operation and chlorite bleaching
Pretepon G, Precolor ekstra
4. Initial washing before bleaching (after mercerization)
CH₃COOH dosage to pH = 5,8 - 6
SINGEING UNIT.
brushing
singeing
padding (CH₃COOH or Na₂CO₃)
alkaline or slightly acidic waste
PAD - ROLL PADDER.
padder (20°C)
moveable reaction tank
periodic waste
small quantity of waste
moveable reaction tank
moveable reaction tank
moveable reaction tank
Positions of moveable reaction tanks. Rotation time 3 h. Small quantity of waste.
1. Extraction bleaching process
NaOH, Na₂CO₃, Precollin B, Ergon B, Na₃PO₄, sulphonated castor oil, Precosolve S
2. Sodium chlorite bleaching process
NaClO₂, NaNO₃, NH₃ aq, HCOOH, wetting agent
TWO STAGE FULL - WIDTH WASHER NO. III.
Processes as washer no. I.

Figure 5-6. Finishing Plant B. Bleach house (con.)

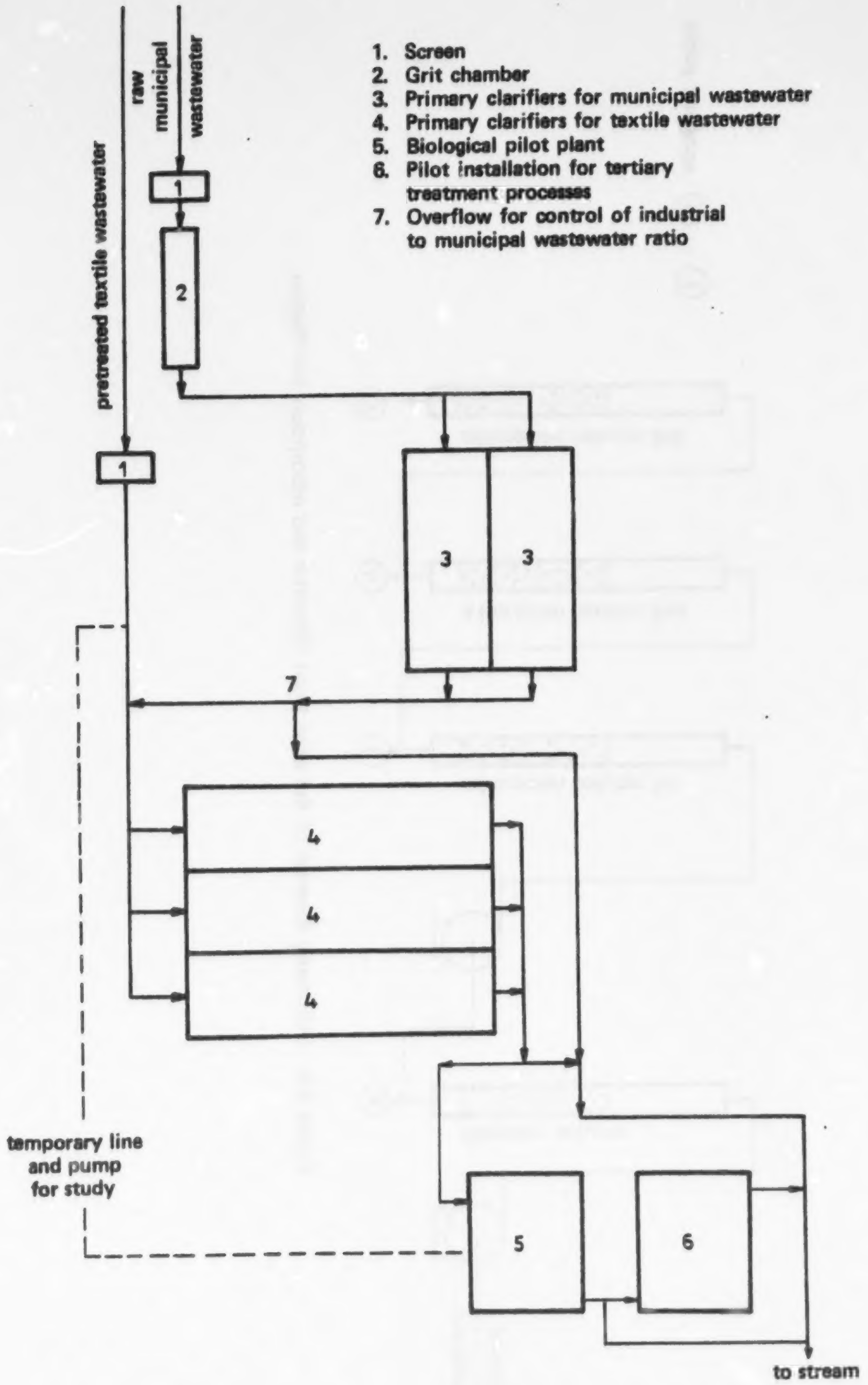

raw
municipal
wastewater
pretreated textile wastewater
1. Screen
2. Grit chamber
3. Primary clarifiers for municipal wastewater
4. Primary clarifiers for textile wastewater
5. Biological pilot plant
6. Pilot installation for tertiary treatment processes
7. Overflow for control of industrial to municipal wastewater ratio
1
2
1
3
3
7
4
4
4
temporary line
and pump
for study
5
6
to stream

Figure 5-7. Schematic plan of the primary treatment plant and the pilot plant in Andrychow.

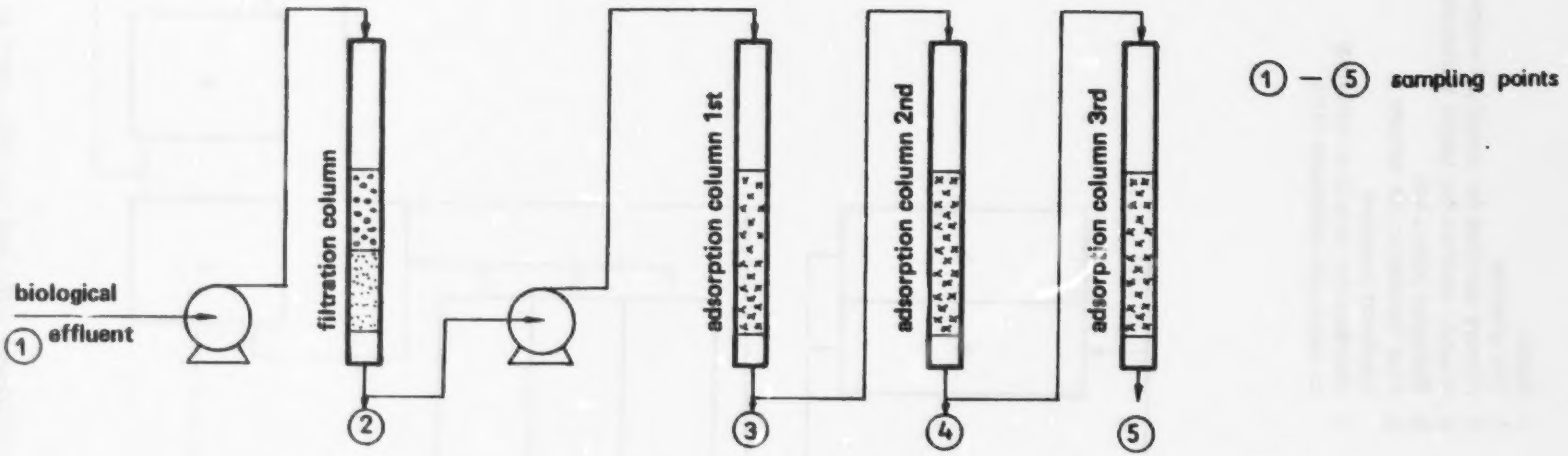

biological
① effluent
filtration column
②
adsorption column 1st
③
adsorption column 2nd
④
adsorption column 3rd
⑤
① — ⑤ sampling points

Figure 5-8. Schematic diagram of the pilot plant filtration and adsorption installation.

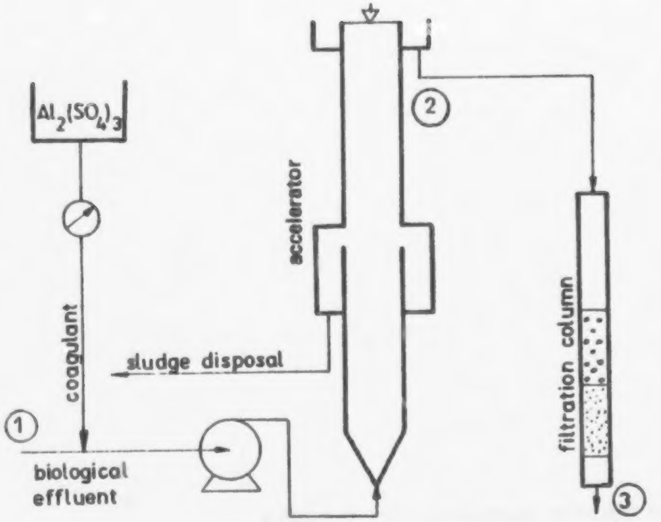

Al2(SO4)3
coagulant
sludge disposal
accelerator
filtration column
①
②
③
biological effluent

Figure 5-9. Schematic diagram of the pilot coagulation installation.

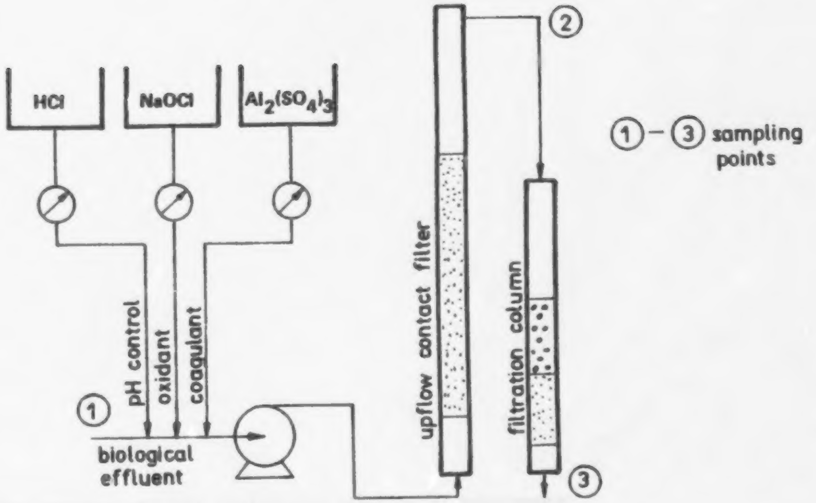

HCl
NaOCl
Al2(SO4)3
pH control
oxidant
coagulant
①
biological effluent
upflow contact filter
filtration column
②
③
① – ③ sampling points

Figure 5-10. Schematic diagram of the pilot upflow filtration installation.

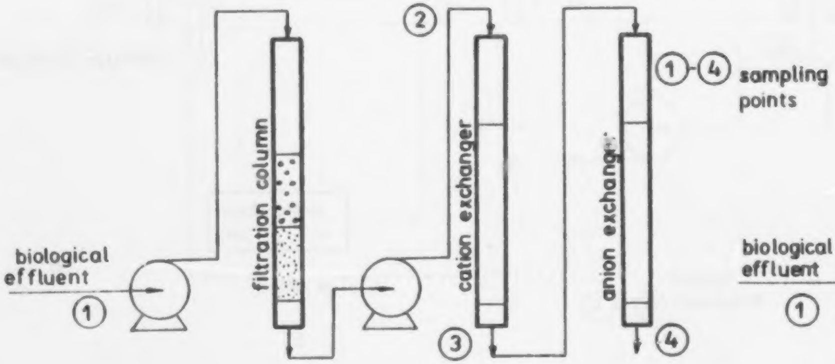

biological effluent
①
filtration column
②
cation exchanger
③
anion exchanger
④
①-④ sampling points

Figure 5-11. Schematic diagram of the pilot ion-exchange installation.

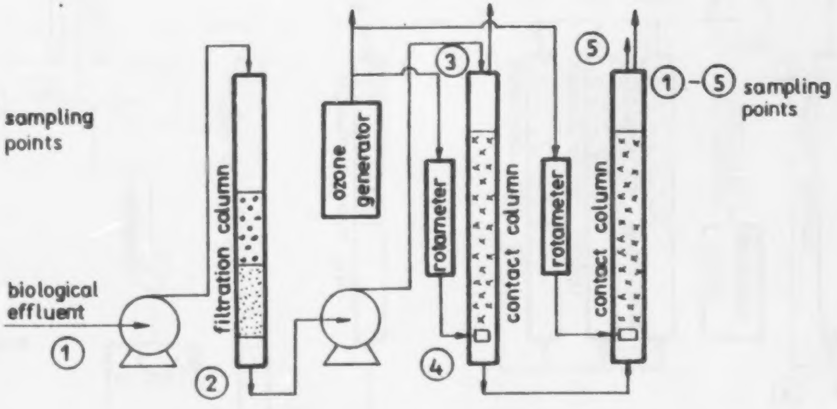

biological effluent
①
filtration column
②
ozone generator
rotameter
③
④
contact column
rotameter
contact column
⑤
①-⑤ sampling points

Figure 5-12. Schematic diagram of the pilot ozone oxidation installation.

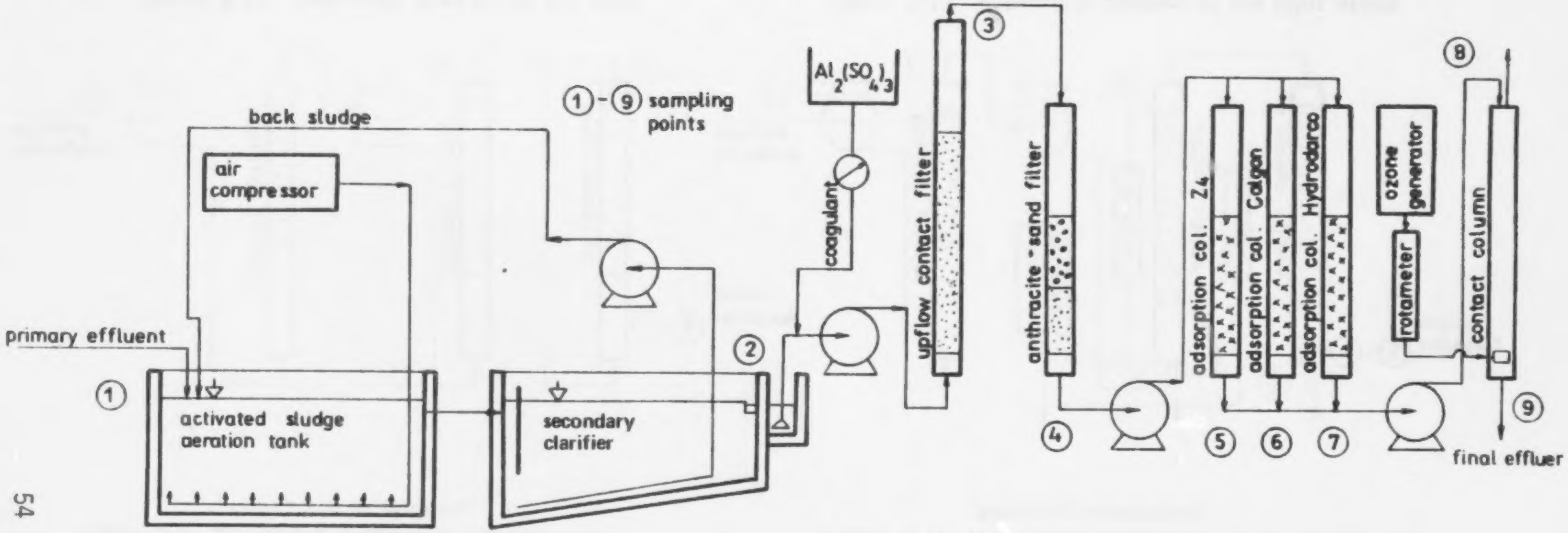
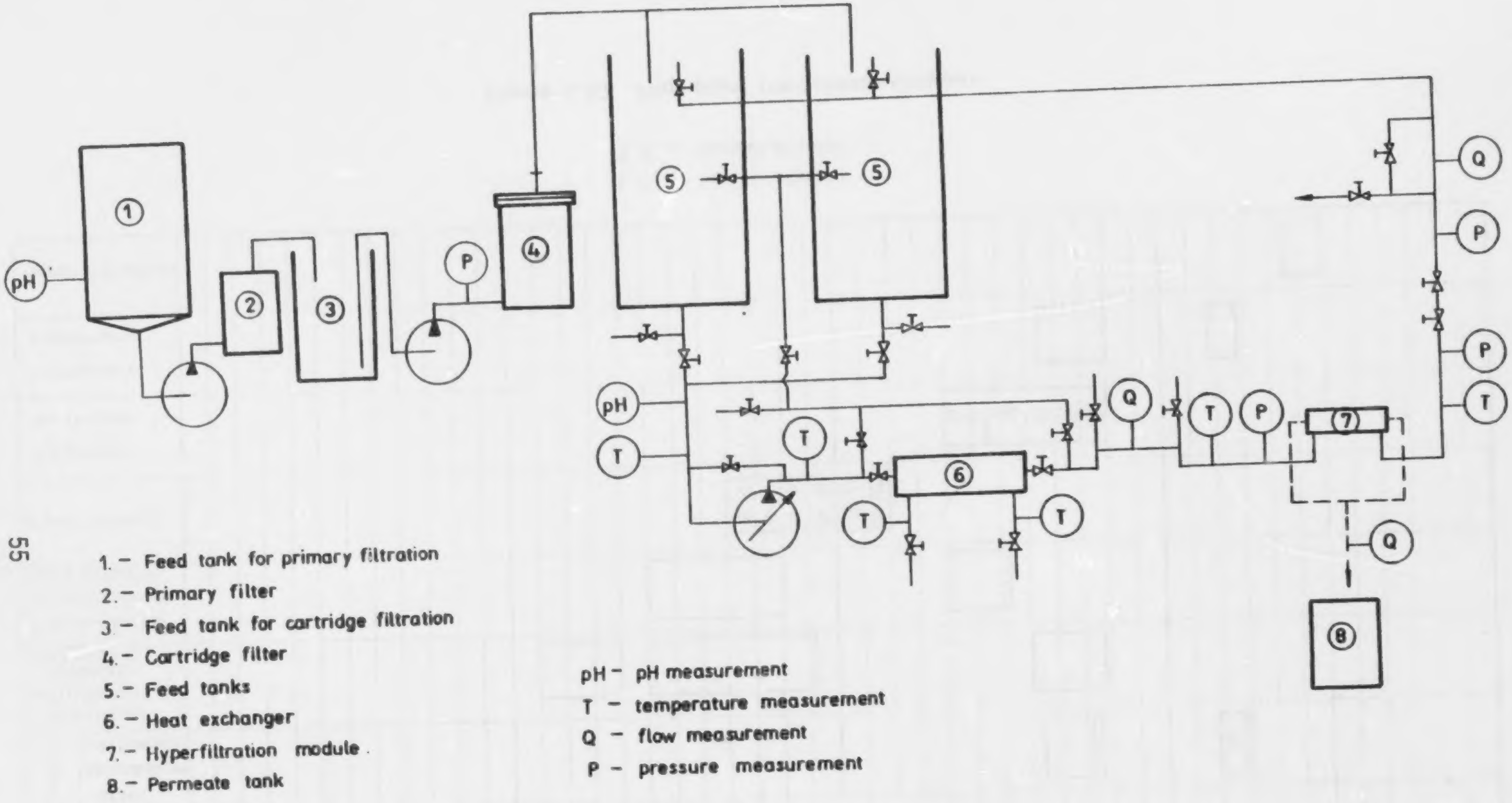

back sludge
① - ⑨ sampling points
air compressor
primary effluent
①
activated sludge aeration tank
secondary clarifier
②
$Al_2(SO_4)_3$
coagulant
upflow contact filter
③
anthracite - sand filter
④
adsorption col. Z4
adsorption col. Calgon
adsorption col. Hydrodarco
⑤
⑥
⑦
ozone generator
rotameter
⑧
contact column
⑨
final effluer

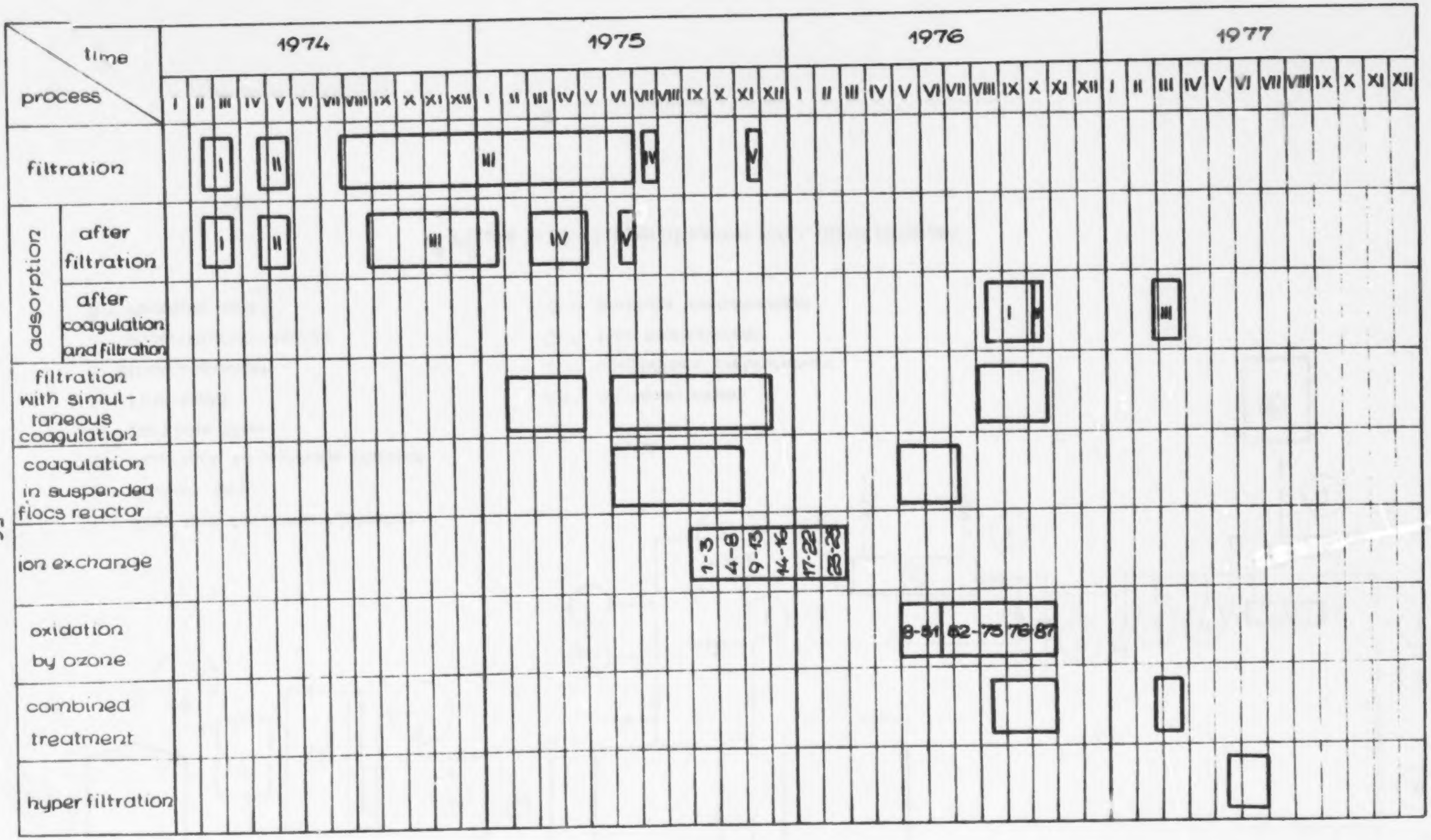
Figure 5-13. Schematic diagram of the pilot installation for combined treatment processes.



1. – Feed tank for primary filtration
2. – Primary filter
3. – Feed tank for cartridge filtration
4. – Cartridge filter
5. – Feed tanks
6. – Heat exchanger
7. – Hyperfiltration module
8. – Permeate tank

pH – pH measurement
T – temperature measurement
Q – flow measurement
P – pressure measurement

Figure 5-14. Hyperfiltration pilot plant diagram.



I, II, ... - number of series

1, 2, ... - number of tests

Figure 5-15. Pilot plant time-phrase diagram.

Table 5-1. Consumption of dyes, chemicals, and auxiliary agents in the Andrychow cotton plant in 1976

No.	Name	Consumption in kg/yr
1.	Sizing agents (Polotex 80, Quicksolan, starch, etc.)	533,453
2.	Wetting agents, detergents (Pretepon G, Sulfonated castor oil, etc.)	145,301
3.	Dispersing agents (Solidokoll K, Matexil FAMIV, etc.)	10,369
4.	Apretting agents (Polopret K-3, Ohobotex FTC, etc.)	538,440
5.	Auxiliary bleaching agents	88,346
6.	Other auxiliary agents (antifoaming, fixing, etc.)	4,880
7.	Sulfur dyes	32,188
8.	Vat dyes	73,517
9.	Indigosol dyes	14,417
10.	Reactive dyes	6,450
11.	Dispersed dyes	45,150
12.	Cottestrense mixed dyes	41,064
13.	Optical whitening agents	10,864
14.	Glacial dyes	1,028
15.	Acid dyes	270
16.	Sulfuric acid (H_2SO_4) 98%	671,090
17.	Acetic acid (CH_3COOH) 80%	196,090
18.	Hydrochloric acid (HCl) 35%	6,430
19.	Formic acid (HCOOH) 85%	8,392
20.	Natrium hydroxide (NaOH) 50%	4,275,840
21.	Liquid glass (Na_2SiO_3)	136,600

Table 5-1 (con.)

No.	Name	Consumption in kg/yr
22.	Common salt ($NaCl$)	242,850
23.	Sodium sulfate (Na_2SO_4)	36,060
24.	Ammonia soda (Na_2CO_3)	122,350
25.	Sodium nitrate ($NaNO_3$)	19,200
26.	Sodium nitrite ($NaNO_2$)	17,200
27.	Ammonia water (NH_3 aq.)	6,505
28.	Sodium bicarbonate ($NaHCO_3$)	3,280
29.	Sodium pyrosulfite ($Na_2S_2O_5$)	6,480
30.	Sodium hydrosulfite ($Na_2S_2O_4$)	165,643
31.	Sodium sulfide (Na_2S)	47,070
32.	Aluminum sulfate ($Al_2(SO_4)3$)	2,100
33.	Magnesium chloride ($MgCl_2$)	8,360
34.	Zinc nitrate ($Zn(NO_3)2$) 35%	4,780
35.	Sodium ortophosphate (Na_3PO_4)	16,980
36.	Sodium acetate (CH_3COONa)	6,980
37.	Hydrogen peroxide (H_2O_2) 30%	612,838
38.	Sodium chlorite ($NaClO_2$)	40,050
39.	Sodium hypochlorite ($NaOCl$)	181,845
40.	Potassium dichromate ($K_2Cr_2O_7$)	47,350
41.	Urea (NH_2CONH_2)	6,800
	Total:	8,434,900

Table 5-2. Activated sludge process, pilot plant, first period

	Average concentration		
	Influent	Effluent	% Removal
BOD_5, mg O_2/l	123	16	87
Dichromate COD, mg O_2/l	255	93	63.5
Permanganate COD, mg O_2/l	64	19	71

Table 5-3. Influent and effluent wastewater quality at Andrychow mechanical-biological treatment plant. Studies carried out after October 10, 1975

	Textile wastes concentration			Concentration of mixed wastes after mechanical treatment			Concentration of mixed wastes after biological treatment			% Removal (biological part)
	Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	
Turbidity - SiO_2 mg/l	1,600	250	686	560	160	350	400	40	217	38
pH	9.0	6.7	-	8.0	6.8	-	8.2	7.5	0	-
BOD mg/l	460	156	315	400	108	209	250	16	48	77
Dichromate COD mg/l	1,500	240	508	1,300	114	300	905	64	93	62
Permanganate COD mg/l	479	112	239	240	58	107	122	21	39	64
Chloride mg/l	208	92	124	85	25	64	81	27	61	-
Sulfate mg/l	1,049	510	782	405	268	361	773	224	475	-
Phosphate mg/l	9.3	0.7	2.9	9.8	1.6	4.8	2.2	0.6	1.3	73
Ammonia nitrogen mg/l	0.56	0.06	0.40	6.72	0.11	1.87	0.56	0.06	0.35	81
Nitrite nitrogen mg/l	6.00	0.80	2.86	0.75	0.02	0.20	1.00	0.07	0.31	-
Nitrate nitrogen mg/l	2.76	0.01	1.32	3.36	0.06	0.90	2.32	0.01	1.01	-
Organic nitrogen mg/l	13.32	0.56	8.38	28.48	4.76	15.61	18.48	0.06	4.72	70
Silica mg/l	2.3	0.4	1.5	9.2	0.4	3.0	7.8	1.0	3.5	-
Calcium mg/l	36	22	30	35	24	29	34	20	27	-
Magnesium mg/l	26.8	1.1	8.3	30.0	1.2	10.8	11.4	0.9	4.4	59
Iron mg/l	5.6	3.6	11.5	11.0	1.4	4.4	4.8	0.1	2.3	48
Nickel mg/l	1.0	0	0.2	0.01	0	0.004	0.1	0	0.02	-
Copper mg/l	5.8	0	1.2	5.0	0	1.06	4.7	0	0.98	-
Zinc mg/l	1.9	0	0.9	1.5	0	0.6	0.9	0	0.4	33
Chromium (total) mg/l	15.00	0.80	5.66	8.00	0.20	3.20	6.00	0.10	1.88	41
Chromium Cr^{+3} mg/l	15.00	0.10	4.45	8.00	0.12	2.45	6.00	0.10	1.76	28
Chromium Cr^{+6} mg/l	4.00	0.16	1.22	1.70	0.08	0.76	0.36	0.00	0.09	88
Total hardness mval/l	2.07	1.85	1.93	2.67	1.28	1.93	2.14	0.86	1.60	-

Table 5-3 (con.)

		Textile wastes concentration			Concentration of mixed wastes after mechanical treatment			Concentration of mixed wastes after biological treatment			% Removal (biological part)
		Maximum	Minimum	Average	Maximum	Minimum	Average	Maximum	Minimum	Average	
Anionic deterg.	mg/l	16.0	6.2	10.1	6.8	4.0	4.8	3.1	0.6	2.3	52
Phenol	mg/l	4.0	0	1.3	0.6	0	0.2	0	0	0	100
Ether extract	mg/l	214.0	8.2	67.3	112.0	8.0	40.3	68.0	0.2	15.8	61
Cyanide	mg/l	0.44	0.02	0.17	0.49	0	0.11	0.28	0	0.09	-
Alkalinity	mval/l	23.2	53	15.0	11.4	2.0	8.3	11.4	2.6	8.5	-
TDS	mg/l	3,674	2,355	3,076	1,742	1,310	1,492	1,432	582	1,143	24
VDS	mg/l	837	534	692	517	312	394	299	134	223	43
Dissolved solids	mg/l	3,140	1,708	2,383	1,340	955	1,098	1,208	424	920	16
TSS	mg/l	228	110	162	302	43	157	91	38	68	57
VSS	mg/l	131	19	79	220	11	108	76	11	41	62
SS	mg/l	114	60	86	63	24	45	37	15	27	40

SECTION 6

FILTRATION PROCESS

INTRODUCTION

Description of the Problem

The sedimentation process does not insure the entire removal of fine particles of suspended matter. Even with properly working secondary sedimentation tanks, approximately 20 mg/l of suspended solids remain. Moreover, in the case of a high variability in the composition of wastewater, which occurs in the treatment of municipal sewage mixed with a considerable portion of industrial wastewater, disturbances resulting from the poor settling properties of activated sludge should be taken into account. These disturbances leave a residue of settlable suspended solids in biologically treated effluent directed to the tertiary treatment or to the receiving water. The increased amount of suspended solids in biologically treated wastewater is particularly undesirable when wastewater is directed to some further tertiary treatment by physicochemical processes such as adsorption, oxidation, or reverse osmosis.

One of the most universal and easiest procedures for removal on nonsettlable suspended solids is rapid-sand or multimedia filtration. In this case, the degree of removal of suspended solids and other pollutants depends on many conditions. No mathematical formula has yet been found to determine the performance parameters of filtration in relation to the composition of wastewater and the required effectiveness. It is necessary to establish criteria for determining the appropriateness of this process and for determining its parameters. The present investigations are a contribution to the establishment of such criteria.

Description of the Process

The filtration process has been applied for a long time to the treatment of water containing suspended solids. When filters are applied for the removal of the suspended solids after chemical precipitation processes, primarily mineral suspended solids are dealt with. However, the filtration of biologically treated wastewater involves mainly organic suspended solids--for example, activated sludge flocs. These suspended solids are separated on a filtration bed through which the wastewater passes. Quartz sand is used most often as a filter medium. Sometimes other materials, such as anthracite or garnet, are used in a multimedia filter. A high rate of filtration of wastewater is most often applied at the rate of from 3 to 25 m^3/m^2h. The suspended solids retained on the bed are washed out with water or with both water and air. The washing process is carried out in a cyclical way at the end of the filter run. The length of the filter run depends on the porosity of the bed and the amount of suspended solids retained. The cycle length is usually limited by the allowable head losses through the filter.

OBJECTIVES

Since many problems have been encountered in the tertiary treatment of municipal sewage combined with textile wastewater, investigations have been undertaken with the following objectives:

- To check possibilities of increasing the effectiveness of biological wastewater treatment by the application of filtration as a final tertiary process,
- to fix the optimum design parameters for the filters, and
- to determine the usefulness of filtration of biologically treated wastewater as a process preliminary to further tertiary physicochemical treatment processes such as adsorption, ion exchange, ozonation, and reverse osmosis.

SCOPE OF INVESTIGATION

Investigations on the one-stage filtration process were carried out using biologically treated municipal wastewater mixed with textile wastewater. The following technological schemes were applied:

- One filtration bed preceding the adsorption column, and
- several filtration columns working in parallel, each having a different filter medium and different hydraulic parameters.

For most investigations, the columns were open.

All the investigations can be divided into two stages:

1. Laboratory scale investigations performed in columns 35 mm in diameter and 1,500 mm high. Enough wastewater was supplied to carry out one filtration cycle.
2. Pilot scale investigations performed in columns 150 mm in diameter. After leaving the secondary sedimentation tank, the wastewater was continuously fed to the columns.

The following parameters were determined:

- Technological effects of the application of single medium and dual media beds,
- optimum filtration rate,
- influence of the wastewater composition on the obtained effects,
- effectiveness of particular filter media applied in the multimedia filtration bed,
- head losses,

- determination of optimum washing parameters, and
- hydraulic characteristics of flow.

PROCEDURE OF INVESTIGATION

Description of General Experimental Conditions

First Stage: Laboratory Scale Investigations--

Experimental installation--Investigations were carried out on an experimental model apparatus (figure 6-1) including bottles containing biologically treated wastewater to be fed, a blower, a dosing tank, filtration columns with equipment, and glass bottles used as receivers of the filtrate. Glass bottles, each of 50 l, were used to store all the biologically treated wastewater necessary for one experimental cycle. A blower was used to raise the wastewater to a 10-l glass bottle used as the upper dosing tank.

Wastewater was fed to the filtration bed by gravity, and the flow was controlled by means of a floating valve. The wastewater surface over the bed was at a constant level. The filtration housing of the column consisted of a glass tube with an inner diameter of 36 mm and a height of 1,500 mm. In the tube, manometers and sampling ports were installed to measure the hydraulic pressure at six levels and to determine the wastewater quality changes at various depths of the bed.

Description of the filtration beds--Anthracite and river quartz sand with natural shape and rounded edges were used as filter media. Two kinds of filter bed arrangements, indicated as A and B, were applied. The supporting layer was 13 cm high and always consisted of gravel with a constant granulation. The filtering layer itself consisted either of sand of varied granulation (variant A) or of sand and anthracite alternately (variant B). A precise description of the filter media applied is given in table 6-1.

Procedure--The laboratory scale investigations involved six filter runs designed to study the effectiveness of the filtration of biologically treated wastewater.

The samples were collected from the secondary sedimentation tanks, each in an amount sufficient to carry out one investigation cycle (assumed to last 12 h). According to the applied rate of filtration, 120 to 350 l of wastewater were sampled. For both kind of beds, the applied filtration rate amounted to 4, 8, and 12 m^3/m^2h. The parameters of the filtration process and the results obtained are listed in table 6-2. Results for tests 3, 4, and 5 are shown graphically in figure 6-2. The pressure versus depth changes during the filtration cycle are shown in figures 6-3 and 6-4.

Sampling--Samples for the analysis of influent wastewater were collected once for each filtration cycle from a portion of wastewater to be fed, whereas samples for the analysis of wastewater after filtration were collected several times from each cycle, the frequency depending on the duration of the cycle (on the average, three samples per cycle).

Scope of physicochemical analysis--Determinations were made of the following pollution indicators in the samples: Suspended solids, BOD_5, dissolved solids, color, dichromate COD, permanganate COD, and detergents. The analyses were performed according to the procedures described in section 4.

Second Stage: Pilot Scale Investigations--

Experimental installation--The pilot scale investigations were carried out on an experimental model installation (figure 6-5) mounted at the pilot plant in Andrychow. The wastewater biologically treated by means of activated sludge was collected from the secondary tank and pumped to the tank situated above the filtration columns. The basic task of the 200-l tank was to compensate for the hydraulic impacts resulting from the periodic work of the pump and to stabilize the pressure at the inlet to the filtration columns. The tank did not equalize the wastewater quality, but it did act as a retention chamber, ensuring a constant supply of wastewater to the filtration columns during periodic operation of the pump. The flow capacity of the pump was 30 l/min.

In the filtration columns, the constant wastewater level was maintained at 0.8 m above the filtration bed by means of a floating valve. Only in the course of the third investigation series did the filtration bed work under the higher pressure generated by the layer of wastewater contained in the filtration column and in the tank. The total wastewater layer height above the bed at that period was 2 m. The height of the bed was always 1 m. The flow rate was controlled by means of a valve installed at the outlet of the column. In the course of the fourth investigation series, a rotameter was mounted at the outlet of the column to continuously indicate the flow intensity.

The filtration columns were equipped with several side tubes with T-connections. The vertical manometer tubes, connected to T-connections, made it possible to continuously observe pressure losses during the filtration. The second outlet of the T-connector terminated with a valve that served to collect samples of wastewater from various depths of the bed.

Description of the filtration beds--Anthracite and river quartz sand with natural shape and rounded edges were used for filtration. The investigations were carried out using single medium sand beds and dual media beds consisting of both sand and anthracite.

A description of the filtration beds applied in individual series and columns is given in table 6-3. For beds B and C, applied for the fourth and fifth investigation series, the sand and the anthracite curves have been plotted. From that diagram, parameters d_{10}, d_{60}, and K_r (figure 6-6) characterizing the bed have been determined. The values determined for the bed of column B are listed in table 6-4. The determination procedure is given later in this section.

The filtration columns were made of Plexiglas tubes with an inner diameter of 150 mm. For the pilot investigations on the filtration process, tubes from 150-mm to 200-mm diameter are most often used [13,14].

As there was a possibility of wall effects exerting influence on the obtained results, measurements of the flow rate distribution in the cross section of the bed were carried out.

The course of investigations--The process of filtration was carried out in such a way as to ensure a continuous supply of filtered wastewater to the adsorption columns. For that purpose it was necessary to adapt the investigation period for particular series of the filtration to the length of the adsorption column operation cycle. The entire investigation cycle of the pilot scale filtration process was performed in five series, the last two of which, besides investigations into the rate of pollutant removal, included measurements of the filtration rate distribution in the bed as well as of the washing parameters of the beds.

The first series lasted from February 12, 1974, to March 23, 1974. The filtration process was carried out on the bed described in table 6-3. The rate of filtration was 5.3 m^3/m^2h, and the maximum head losses were 900 mm of water depth. The length of one filtration cycle was on the average 12 h. The process was carried out continuously for 24 h with a half hour break for washing, performed at the moment when the losses reached their maximum assumed value. The washing was done with municipal water. The results are listed in table 6-5.

The second series was carried out simultaneously with the second adsorption series from April 26, 1974, to May 25, 1974. The difference between these series consisted in a longer cycle of filtration, amounting to 23 h on the average, caused by increasing the value of head losses from 900 mm up to 1,800 mm of water depth. The same procedure and the same parameters of the filtration process that were used in the first series were applied here. The results are listed in table 6-6.

The third series was carried out on one column in the period from August 28, 1974, to June 30, 1975, with breaks for exchanging the adsorption beds. This filtration series was concurrent with the third, fourth, and fifth adsorption series. In this third series a dual media filtration was applied. The filtration results are listed in table 6-7.

The fourth series was carried out simultaneously in four columns with various beds and various filtration parameters (table 6-8). Each cycle of filtration was investigated separately, and the sampling and measurements were taken from the beginning to the end of the cycle. The cycles were started in all the columns at the same time, usually about 10 o'clock. At the beginning and in the middle of the cycle the effectiveness of the removal of suspended solids from each bed layer was checked. Every hour the head losses at all hydraulic gradient lines were recorded. Pressure versus depth changes during the filtration cycle are shown in figure 6-13

The fifth series was carried out in one column. The characteristics of the bed and the parameters of the filtration are given in table 6-3. These investigations were carried out to check the results obtained in the fourth series, and the observations were made in the same way as those in the fourth series. Four filtration cycles took place. Contaminant removal data from the first two cycles are given in table 6-9. The investigations concerning the flow rate distribution in the bed cross section that were made in the course of the fourth series were repeated here. Measurements of the washing parameters were also taken.

Sampling--The method of sampling depended on the procedure and objectives assumed for particular series. For the first through third series the samples were collected from the filtration column influent and effluent every hour simultaneously. Then the daily average sample was composed.

If the washing of the filtration columns occurred at the time of sampling, the effluent sample was collected after the filtration column had been put to work again. In the fourth and fifth series samples were taken at various periods during the filtration cycle. Samples were taken at the following time intervals, counting from the beginning of the cycle: 30 min, 60 min, 90 min, 120 min, and afterwards every 120 min until the termination of the cycle. The samples were taken from the influent and from the effluent at 5-min intervals. A part of each sample was used for the preparation of one average sample from the entire cycle, and the remaining part was used to determine the suspended solids separately for every individually collected sample. Additionally, in several cycles of the fourth and fifth series the samples were collected at various levels of the bed at the beginning and the middle of the filtration cycle. The washing water samples were collected from the final portion of washing water after all the water used for washing the bed had been mixed.

Physicochemical analysis--For the daily average samples combined for the entire 24 h, the following indicators were determined: pH, alkalinity, oxygen, permanganate, BOD_5, COD, suspended solids, and color. Twice a week detergents were determined. For all samples taken at random, only suspended solid determinations were made. The analysis was conducted according to the procedure described in section 4.

Determination of physical properties of the anthracite and sand--Bulk density was determined as follows. Using dry cylinders of 250-ml capacity, the sand or anthracite was compacted to a constant level of 200 ml. Next, the contents were weighed within 0.01-g accuracy. The bulk density (weight by volume) was calculated from the formula:

$$x = \frac{G}{200}\ \text{g/cm}^3$$

where

G = the bulk of the anthracite contained in the cylinder, in g.

Porosity was determined as follows. Cylinders 250 ml each were filled with 100 ml of water, and the sand or anthracite that had previously been weighed was slowly poured in. Then the volume of the mixture was read. The pore space in percentage was calculated according to the formula:

$$p = \frac{a_1+a_2-a}{a_1} \times 100 = \frac{200+100-a}{200} \times 100$$

where

a = volume of sand and water mixture in ml,

a_1 = volume of sand in ml, and

a_2 = volume of water in ml.

The specific gravity in g/cm^3 was calculated from the formula:

$$S.G. = \frac{\text{bulk density}}{100-p} \times 100 \text{ g/cm}^3.$$

Measurements of the flow rate distribution in the filtration bed--The measurements were carried out using the tracer technique to determine the flow time of colored wastewater. The coloration of the wastewater was obtained using a 1 percent solution of vat dye, that is, of helanthrene green. About 2.5 l of the dye solution were fed in directly over the filtration bed. The penetration time of the solution through the bed was observed and measured.

During the fourth series an analysis was conducted to choose the right kind and amount of dye, as well as to make observations of its penetration through the bed and to measure the trace flow time through all the bed layers. The observations were carried out for both clean and contaminated beds in columns A, B, and D, with the assumed filtration parameters maintained (table 6-3). In the course of the fourth series, the coloration of wastewaters and the observations were repeated twice exclusively for bed C. Flow velocity of 5 m^3/m^{2}h was applied. The penetration of the colored wastewater wave through particular bed layers was observed. The penetration time was measured and samples were collected simultaneously every 20 sec from the second and fourth measurement levels (figure 6-5), as well as from the effluent from the column. For these samples the concentration of color was determined.

Measurements of washing parameters--In the fifth series, investigations were carried out into the method and parameters of washing in relation to the length of the filtration cycle. These investigations were performed on a dual media filtration bed with granulation, as in the curves shown in figure 6-6.

The filter bed was washed either only with tap water [22,27] or with tap water and air alternately [21,23]. The temperature of the washing water was kept constant at 8° C. Washing water and air were supplied upwards from the bottom of the filter, and washings were discharged through the outlet 0.9 m above the bed surface reservoir of a known volume.

The following parameters were measured during the washing period:

- Time of washing--the time during which the washing medium is applied (the washing was terminated at the moment when the difference in turbidity of the washing water between the inlet and outlet was negligible);

- intensity of washing--calculated from the formula:

$$i = \frac{g}{F} \times \text{m}^3/\text{m}^2\text{h}$$

where

g = consumption of air or water per unit of time measured by rotameters in m^3/hr, and

F = the surface of beds in m^2;

- amount of washing medium:

$$Q = g \times t \text{ in m}^3 \text{ where } t = \text{washing time in h};$$

- expansion of the bed--the height of each of the bed layers was read on the expansion scale and the percentage increase during the washing was calculated;
- amount of suspended solids removed--the concentration of suspended solids in the total amount of washing water was determined analytically, and then the amount in kg was calculated.

The bed-washing parameters applied are specified in table 6-9. The average intensity of bed washing was applied in a value capable of maintaining constant expansion of the bed in one washing period. The maximum intensity of bed washing was applied so as to insure that anthracite particles not be ejected from the column, thus causing a decrement of the bed [29]. The applied intensity of washing with water ranged from 58.5 $\text{m}^3/\text{m}^2\text{h}$ with 25 percent expansion of sand and 70 percent expansion of anthracite, to 107 $\text{m}^3/\text{m}^2\text{h}$ with 40 percent expansion of sand and 80 percent expansion of anthracite. The bed washing intensity applied by means of air was constant at 105 $\text{m}^3/\text{m}^2\text{h}$. In the course of washing, the partial mixing of the sand and anthracite layers was observed.

METHOD OF INTERPRETING RESULTS

The assessment of the effectiveness of the filtration process was based on determinations of the suspended solids and BOD_5 concentrations. For wastewater before and after the filtration process and for the removal amounts, these indicators have been given in percentage.

A statistical method was used to interpret the values of the pollution parameters listed in tables 6-5 through 6-7. The probability percentage was calculated from the formula:

$$P_i = \frac{M(i-1)}{n} \times 100 + \frac{1}{2}\,\frac{M_i - M(i-1)}{n} \times 100$$

where: i is the successive interval (the chosen interval value = 1.00 mg/l);

M is the cumulative number of cases through the given interval M_i; and

n is the overall number of cases in the series.

The P_i value is on the scale drawn for the normal distribution, according to the Gauss curve (figures 6-7 to 6-10).

The values whose probability of occurrence was lower than 15.87 percent or higher than 84.13 percent [29] were rejected as uncharacteristic. The value with 50 percent probability of occurrence was accepted as average. For all the series, this value was approximated to the arithmetic mean of the results. Moreover, a deviation constant was calculated for characteristic probability points. For indicators less important for the filtration process, only the arithmetic average values were calculated.

DISCUSSION OF RESULTS

Effectiveness of Filtration

The filtration effectiveness of biologically treated wastewater has been most often evaluated by analyzing removal of contaminants determined by such indicators as suspended solids, BOD_5, and COD [23]. In the present investigations, the contaminants characteristic for textile wastewater--color and detergents--were also determined. The removal most often achieved in the process of filtration varies from 70 percent [17] to 98 percent [25] for suspended solids, and from 67 percent [21] to 99 percent [23] for BOD.

The concentration of suspended solids in wastewater after the filtration process preceded by conventional activated sludge treatment should be, according to Culp [13], 3 to 10 mg/l. The effects obtained in the present investigations do not always fall within the ranges given above. This can be seen distinctly especially in the first series when the BOD and suspended solids average removal obtained were scarcely 29 and 34 percent, respectively (figures 6-8 and 6-7). However, at the same time, the suspended solids content in the effluent was not high, amounting to a mean of 10.4 mg/l.

In the remaining series, the removal was higher, amounting on the average for suspended solids to 67 percent in the second and third series (figures 6-9 and 6-11), and to 77 percent and 83 percent in the fourth and fifth series (tables 6-8 and 6-9). The average BOD removal totalled 62 and 61 percent in the second and third series (figures 6-10 and 6-12), and 35 percent in the fifth series (table 6-9). The removal of the remaining indicators was very irregular in all the series. The average COD removal for the first three series amounted to 32.6 percent, removal of detergents to 29.3 percent, and average color removal to 15.9 percent (table 6-7).

The wide range of effects obtained resulted from many factors. The most important are the quality of the influent wastewater, the structure and granulation of the bed, the degree of bed clogging and the duration of the filter cycle, and hydraulic factors such as flow rate value and velocity distribution in the bed cross section. The influence of the individual factors is discussed below.

Influence of the Quality of Wastewater Supplied on the Results--

The influence of the properties of the wastewater supplied to the filtration process is a complex phenomenon, depending both on the concentration and structure of the contaminants and on the performance of the filtration process.

In the Andrychow pilot plant, wastewater is biologically treated in an experimental chamber with a small sludge retention (chamber volume = 16 m^3). This results in frequent variations both in the loading of sludge and in its settling ability, expressed by the sludge volume index. It should also be emphasized that the method of removing sludge from the secondary sedimentation tank is not fully sufficient, for the sludge periodically floated on the surface, causing an increase in the suspended solid content in the effluent. Normally, the sludge volume index ranged from 150 to 400 cm^3/g.

In the first series the suspended solid concentration (in the range $\pm\alpha$) in the influent to the filters fluctuated from 9 mg/l to 22 mg/l, amounting on the average to 16 mg/l (figure 6-7). The concentration (in the range $\pm\alpha$) of suspended solids in the effluent after filtration was 5 mg/l to 16 mg/l, with an average of 11 mg/l. The removal was from 9 to 60 percent, averaging 34 percent (figure 6-7).

In the course of the second series, sedimentation disturbances resulted in an increase in the suspended solid content in wastewater supplied to the filtration process. Suspended solids totalled from 21 mg/l to 61 mg/l, while the average was 42 mg/l (figure 6-9). These disturbances were clearly reflected in the removal percentages on filters, which at this period ranged from 44 to 86 percent--65 percent on the average. The percentage removal of suspended substances had more than doubled. To a much smaller degree, this increase influenced the concentration of suspended solids in the effluent. Then the average content of the suspended solids in relation to the first series increased in the second series by only 30 percent amounting to 14 mg/l.

In the course of the third investigation series the improvement of the obtained effects was undoubtedly influenced by the change in the filtration bed structure, which will be described later.

During these investigations, the expected mathematical dependence between the suspended solids content in the supply of wastewater and the percentage removal of these substances was not found, though it was obtained during research in Chicago [24,25] and in Klimzowiec, Poland [14]. It has been stated that this dependence is variable but, as has been shown in tables 6-5, 6-6, and 6-7, the content of suspended solids in the effluent increases as their content in the supplying influent increases. In order to define this dependence, the suspended solids content was measured and determined every 2 h in both the influent and the effluent, in the course of two cycles within the fourth and fifth series. The results are presented in figures 6-14 and 6-16. Retention of suspended solids occurs mainly in the upper layer of the bed. The influence of cycle time on the course of suspended solids removal could not be determined definitely (figure 6-15).

For BOD_5 loading, the correlation between the wastewater influent to the filtration and the effluent was higher than the same correlation for suspended solids. This dependence value was, however, variable for each of the series, and no mathematical formula for it has yet been found. It was probably caused by the different structures of the contaminants supplied. For other contaminants such as COD, detergents, and color, no interdependence between the degree of removal and the concentration in the influent was found.

Influence of Bed Characteristics on the Removal of Contaminants--
The characteristics of the bed have an essential influence on the effects obtained in the filtration process [27]. A very important bed property is granulation. Brummel [22] states that for suspended solids like activated sludge particles, whose volume is large in relation to weight, it has proved advantageous to apply a bed consisting of several layers of different granulation. This method insures uniform distribution of the retained suspended solids through the entire depth of the bed, resulting in the equalization of head losses and in the prolongation of the filtration cycle. In order to avoid intermixing of the media layers during the washing procedure, materials with different specific gravities were applied--in this case, sand and anthracite.

The laboratory scale investigations carried out in the first stage on the beds described in table 6-1, showed that at very low filtration rates suspended solids and BOD_5 loads were more effectively removed on a single medium filter despite the fact that the bottom layer of dual media filter had particles of a finer granulation. Some authors [15,16] stress that the granulation influence is eliminated by the plugging of the bed, which probably occurred in this case at a low rate of flow ($4\ m^3/m^2h$), which caused an increase in removal on a single medium filter. At the higher flow rate ($12\ m^3/m^2h$), however, the removal of contaminants was considerably higher when a dual media bed with finely granulated bottom layer particles was applied.

Efforts to confirm the above results in the course of the pilot scale investigations did not yield significant results because of great variability in the concentration of wastewater. This has been discussed in preceding sections. Nonetheless, the results obtained at a flow rate higher than $5\ m^3/m^2h$ confirm the greater filtration efficiency of a dual media bed as regards both technological and economic indicators. Better average results were obtained from filtration on the dual media filter (third series) than on the single medium filter (first and second series). This is expressed in the lower concentration of contaminants in the effluent from the column, along with the high removal percentage.

From a comparison of the effects obtained from filtration carried out simultaneously on single and dual media filters (fourth series), it is clear that the suspended solids are better removed on a dual media filter at a constant flow rate 5.1 m^3/m^2h and with the same granulation of the bottom layer media. Probably one of the factors causing the decrease in filtration effectiveness on a single medium filter is the breakthrough of the suspended solids at the end of the cycle.

The probability of outflow of suspended solids is confirmed in column C of figure 6-17, which shows that at the beginning of the filtration cycle the suspended solids are not only retained in the upper layer, but also penetrate into the lower portion of the bed; in the second part of the cycle this penetration decreases.

The influence of the dual media granulation was checked on a pilot scale in the course of the fourth series of investigations, where two columns (A and B) of different bed granulation worked simultaneously at the flow rate of 5.1 m^3/m^2h. In column A, which had a finer bed granulation, the average removal of BOD and COD was higher than in column B (table 6-8). The content of these contaminants and suspended solids in the effluent was also lower in column A. This was especially distinct for suspended solids in the samples collected at the end of the filtration cycle (figure 6-14).

The lower rate of removal at the end of the cycle in the column with fine size media can also be observed in figure 6-14, where the value of the suspended solids content is higher in the middle of the cycle than in the beginning. But with a coarser size filter media and at a higher rate of filtration, removal is better during the second half of the cycle.

Influence of the Filtration Rate--

The investigation carried out in Minworth [26] showed that the changes in the filtration rate in the interval from 4.6 to 25 m^3/m^2h have no essential influence on the efficiency of suspended solids removal. However, Wood [18] has stated that, in investigations at the Maple Lodge Treatment Plant, the removal of suspended solids decreases at filtration rates above 10.2 m^3/m^2h. In Lublinow [19], it has been shown that changing the filtration rate in the range between 5 and 9 m^3/m^2h has no influence on contaminant removal.

The influence of the filtration rate on the process effectiveness was checked on a laboratory as well as on a pilot scale. In laboratory investigations a lower degree of suspended solids removal at a higher rate of filtration in a single medium filter was clearly found. For the removal of remaining indicators, this dependence was not so clear. No distinct influence of the filtration rate was found in a dual media filter either (table 6-2). For the dual media column, in the course of pilot scale investigations, the influence of the filtration rate was checked again and the rates of 5.1 and 15 m^3/m^2h were applied simultaneously. Figure 6-14 provides a diagram of the content of suspended solids in the course of one cycle.

As can be seen from a comparison of curves plotted for column B working at the rate of $V = 15.3$ m^3/m^{2}h, and for column C working at the rate of $V = 5.1$ m^3/m^{2}h, the increase of the filtration rate causes wide fluctuations in suspended solids removal. The average content of suspended solids in the effluent from column A was 8.7 mg/l and from column C was 6.1 mg/l.

The influence of filtration rate on head loss is shown in figures 6-3, 6-4, and 6-13. For a single medium filter, an increase in filtration rate caused an increase in head loss in the upper filter layer. As a result, in the second part of the filtration cycle negative pressure appeared (figures 6-3 and 6-13d). For a dual media filter, an increase in filtration rate caused a small head loss with a distribution relatively uniform through the whole bed (figures 6-4 and 6-13b). Figure 6-13b shows that, below the greater filtration rate, the bed absorptiveness is steadily exhausted. However, the passage of some suspended solids through the bed layer of column B to the effluent increases as the filtration rate increases.

Influence of the Bed Compactness on Contaminant Removal--
In the fourth and fifth series of investigations, the content of the suspended solids was determined for samples collected in various parts of the filtration cycle. On the basis of the results presented in figures 6-14 and 6-16, it is not possible to find an increase in removal effects at the end of the filtration cycle. Moreover, the content of the suspended solids in columns A and B was higher in the second half of the filtration cycle than at the beginning and in the middle of the filter run (figure 6-15). Only column C is an exception (figures 6-17 and 6-15), working at the rate 5.1 m^3/m^{2}h.

Hydraulic Characteristics

On the basis of the measurements recorded in figures 6-18 and 6-19, it can be stated that flow through the filtration column 150 mm in diameter occurred evenly in the whole section. The maximum concentration of indicator in individual layers lasted close to the theoretical flow time. For the anthracite layer the real flow time coincided with the theoretical time, but the flow through the sand layer lasted somewhat longer than the theoretical time. The nonappearance of indicator in a large concentration in a time considerably shorter than the theoretical time is proof that short circuits did not occur on the walls of the column. The flow time through the whole bed at the peak indicator concentration was only 4 to 6 percent shorter than the theoretical time, showing that small dead spaces occurred. The duration of the outflow of the colored wave containing 80 percent of the indicator mass was 1.83 min, which is 35 percent of the theoretical flow time. Therefore, the flow can be regarded as correct.

Filter Backwashing

The backwashing time was variable and depended closely on the procedure and intensity of washing. The backwashing of a filter both with water only, and with air in the middle of the washing period, required long washing times amounting to 9.25 min and 10.4 min, respectively. The shortest filter backwashing times occurred when both the air and the water washing systems were applied.

At a high intensity of bed backwashing, amounting to 107 m^3/m^2h for water and 105 m^3/m^2h for air, the total washing time (table 6-10) was only 5.5 min. But the intensity was so high that there was a danger of the anthracite being ejected and causing the decrement of the bed as well as necessitating constant monitoring of the process [19]. At an intensity of backwashing of approximately 60 m^3/m^2h for water and 105 m^3/m^2h for air, at which there was no danger of bed particles being ejected, the time of washing was 8.5 min. With this system of backwashing, the least water consumption was observed in relation to:

1. The filter wastewater amount--At the washing intensity of 107 m^3/m^2h this proportion was 5.35 percent, and at 58.5 m^3/m^2h it was 6.45 percent. However, when the bed was washed only with water, water consumption in relation to the volume of the filtrate increased to as much as 10 percent.
2. The surface of the filter--This value amounted to 3.95 m^3/m^2 of the bed at the intensity of 58.2 m^3/m^2h and to 4.52 m^3/m^2 at the intensity of 107 m^3/m^2h. When the bed was washed only with water, water consumption increased considerably, to as much as 10.1 m^3/m^2. After the air-water washing, the highest concentration of suspended solids in the washings was observed, indicating that a quick and intensive washing of the bed took place.

When the filtration bed was washed only with water, a conglomeration of the filter media and the ejection of some parts of them were noticed. These effects did not occur at all or occurred only to an insignificant degree when air-water washing was applied. In the course of the washing, a mixing of the sand and the anthracite took place at the limit of the layers over a height of 0.35 m.

Considerable differences in the bed expansion were observed, depending on the media supplied. The greatest expansion of the bed allowed was 40 percent for the sand and 80 percent for the anthracite, occurring while the water was being washed at the intensity 107 m^3/m^2h.

CONCLUSIONS

1. The investigations show that the filtration of biologically treated wastewater reduces the concentration of suspended solids to approximately 10 mg/l, which results in 30 to 75 percent removal (in the range of $\pm\alpha$) of the wastewater BOD. Contaminants characteristic for textile wastewater--COD, color, and detergents--are eliminated only to a small degree and in a very irregular way.

2. The structure of the sludge in biologically treated wastewater has great influence on the quality of the filtered wastewater. When the activated sludge is greatly disintegrated and has poor settling properties, the amount of suspended solids in the filtered wastewater increases. This occurs to a significantly smaller degree than in wastewater which has been only biologically treated, but when the sludge volume index exceeds 100, a concentration of suspended solids over 10 mg/l can be expected.

3. It has been found that a dual media filter is more effective than a single medium filter for biologically treated wastewater. The dual media filter insures a better elimination of suspended solids. Moreover, it allows for a long filtration cycle of 23 to 36 h, in contrast to the 3.5 to 23.5-h filtration cycle obtained with a single media filter. The length of the filtration cycle depends not only on the concentration, but also on the structure of the suspended solids. A determination of the exact dependence would require detailed study of the sediment structure.

4. Studies on the influence of the granulation of a dual media bed on the filtration process show that:

   - A dual media bed with an anthracite layer of 0.5 to 0.75 mm and a sand layer of 0.4 to 0.75 mm gives better removal of suspended solids during a short cycle and at low filtration rates.
   - However, a dual media bed with a granulation of anthracite equal to 1.5 to 2.0 mm, and of sand equal to 0.75 to 1.5 mm, is more economical. Such media sizes insure a long cycle of filtration (36 h). Removal of suspended solids is somewhat lower than with the bed of finer granulation, but it occurs more uniformly throughout the whole cycle.

5. Increasing the filtration rate up 15 m^3/m^2h resulted in a deterioration of the effects because of greater irregularity in the removal of contaminants, especially in the case of media of very fine granulation. A rate of filtration up to 8 m^3/m^2h has been found best from an operational standpoint for the Andrychow wastewater.

6. No positive influence of bed clogging on the obtained effects was found, probably because of the structure of the retained suspended solids.

7. The 150-mm diameter of the filtration column was satisfactory for the pilot scale investigations. The investigations showed that wall effects have no essential influence on the distribution of velocity in the crosssection of the column.

8. A combined backwashing of beds with air and water proved to be most economical. The following washing parameters are regarded as optimum:

   for air: V_a = 100 m^3/m^2h; t = 1 min

   for water: V_w = 60 m^3/m^2h; t = 7 min.

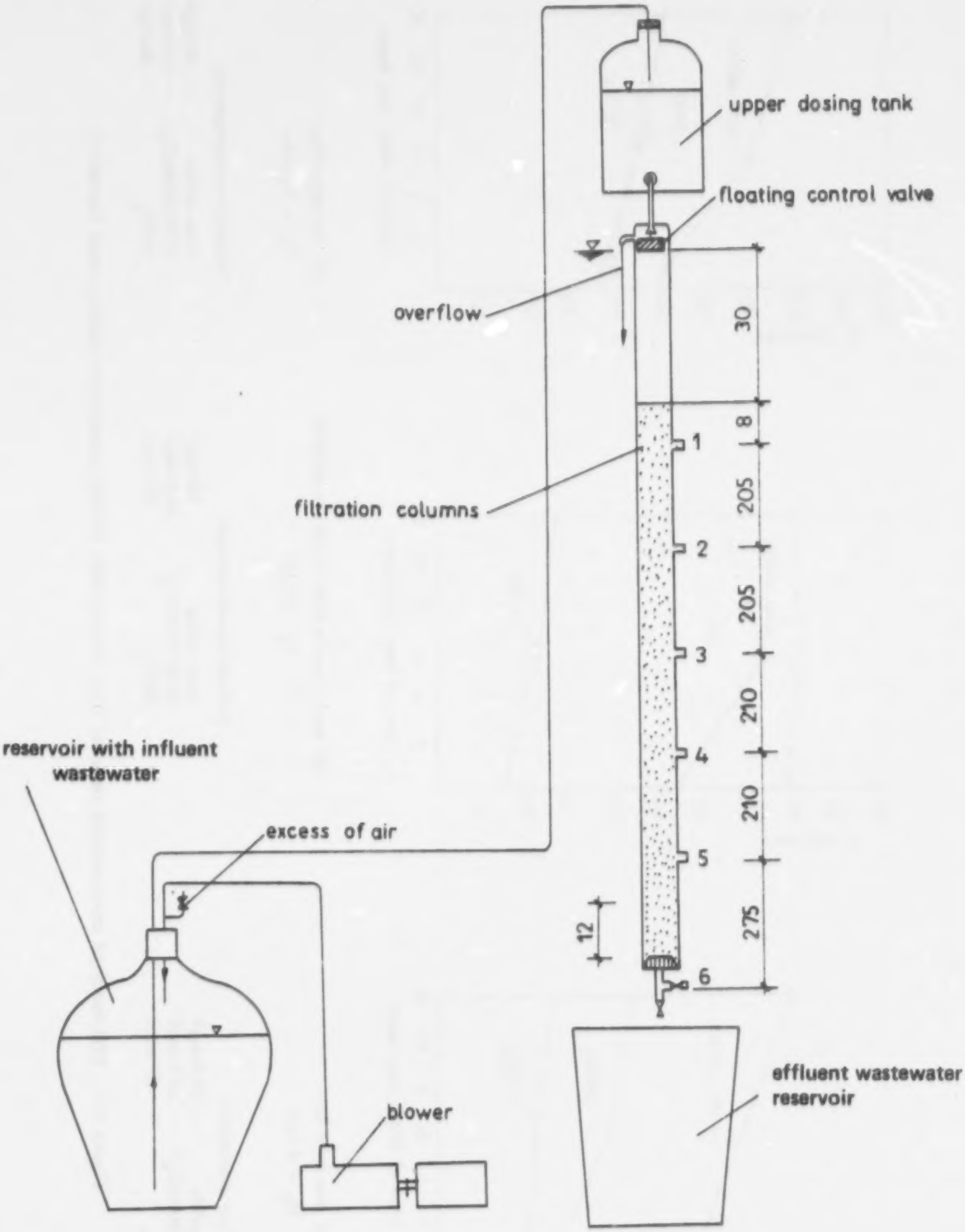
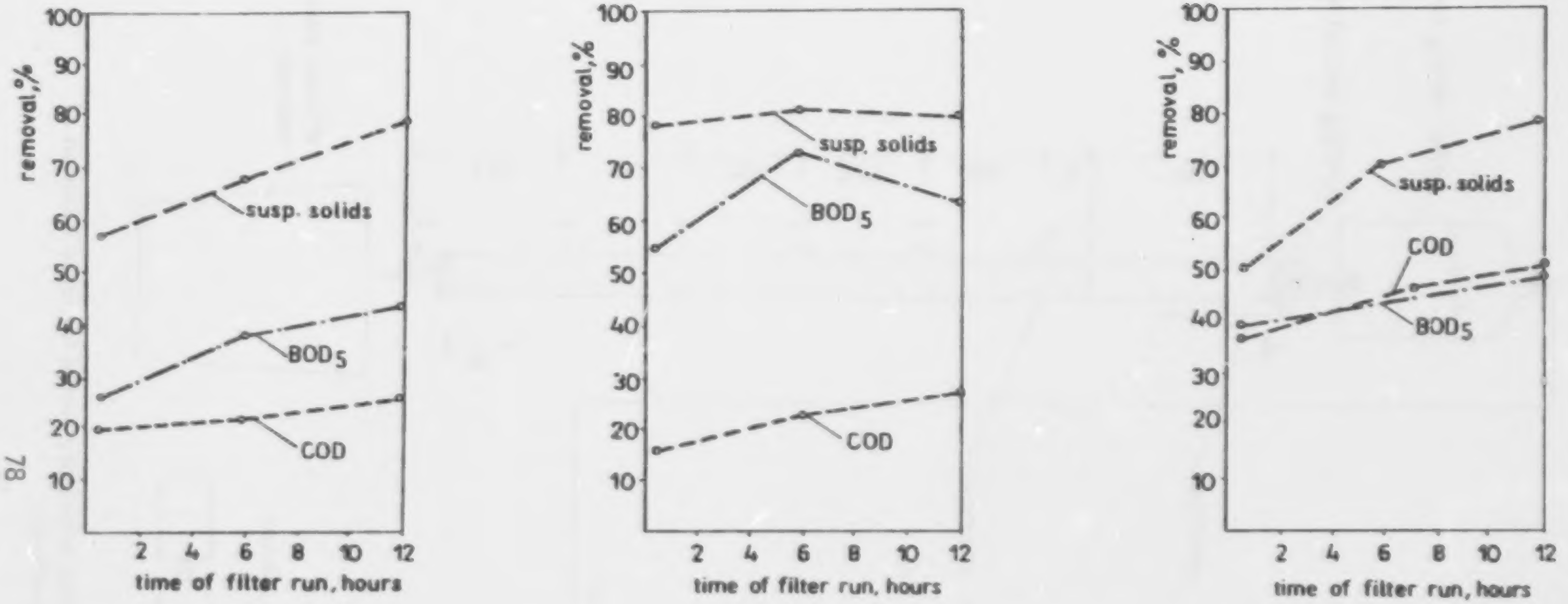

upper dosing tank
floating control valve
overflow
filtration columns
reservoir with influent wastewater
excess of air
blower
effluent wastewater reservoir
30
8
205
205
210
210
275
12
1
2
3
4
5
6

Figure 6-1. Experimental laboratory model for rapid filtration of secondary effluent.



a) one layer filter
V_f = 8 m/h

b) two – media filter: sand + anthracite
V_f = 8 m/h

c) one layer filter
V_f = 12 m/h

Influent concentrations:

susp. solids – 22.8 mg/l
COD ($KMnO_4$) – 22.5 mg/l
BOD_5 – 27 mg/l

Influent concentrations:

susp. solids – 50 mg/l
COD ($KMnO_4$) – 18.5 mg/l
BOD_5 – 22 mg/l

Influent concentrations:

susp. solids – 34 mg/l
COD ($KMnO_4$) – 9.0 mg/l
BOD_5 – 20 mg/l

Figure 6-2. Efficiency of contaminant removal from biologically treated wastewater during rapid filtration.

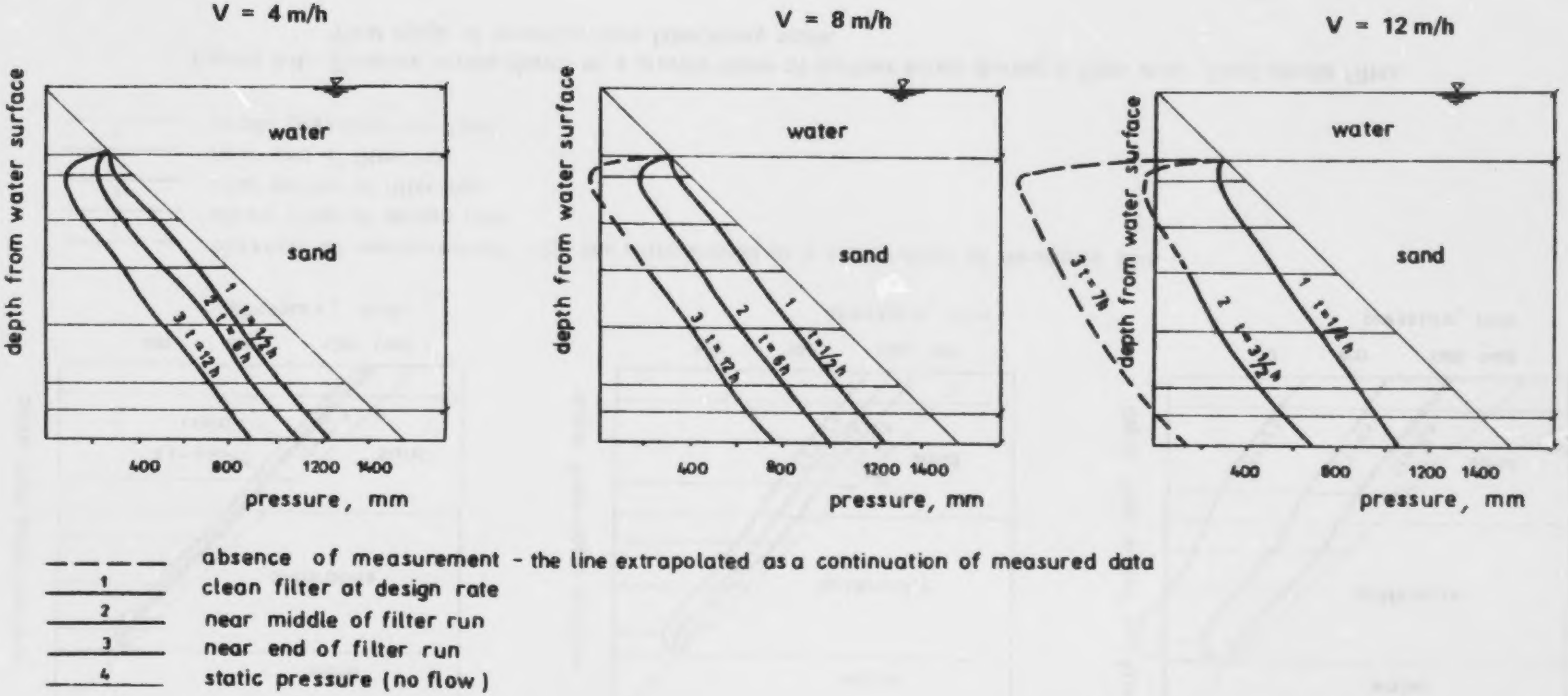


Figure 6-3. Pressure versus depth in a gravity filter at various times during a filter run. Single medium filter. First stage of investigations laboratory scale.

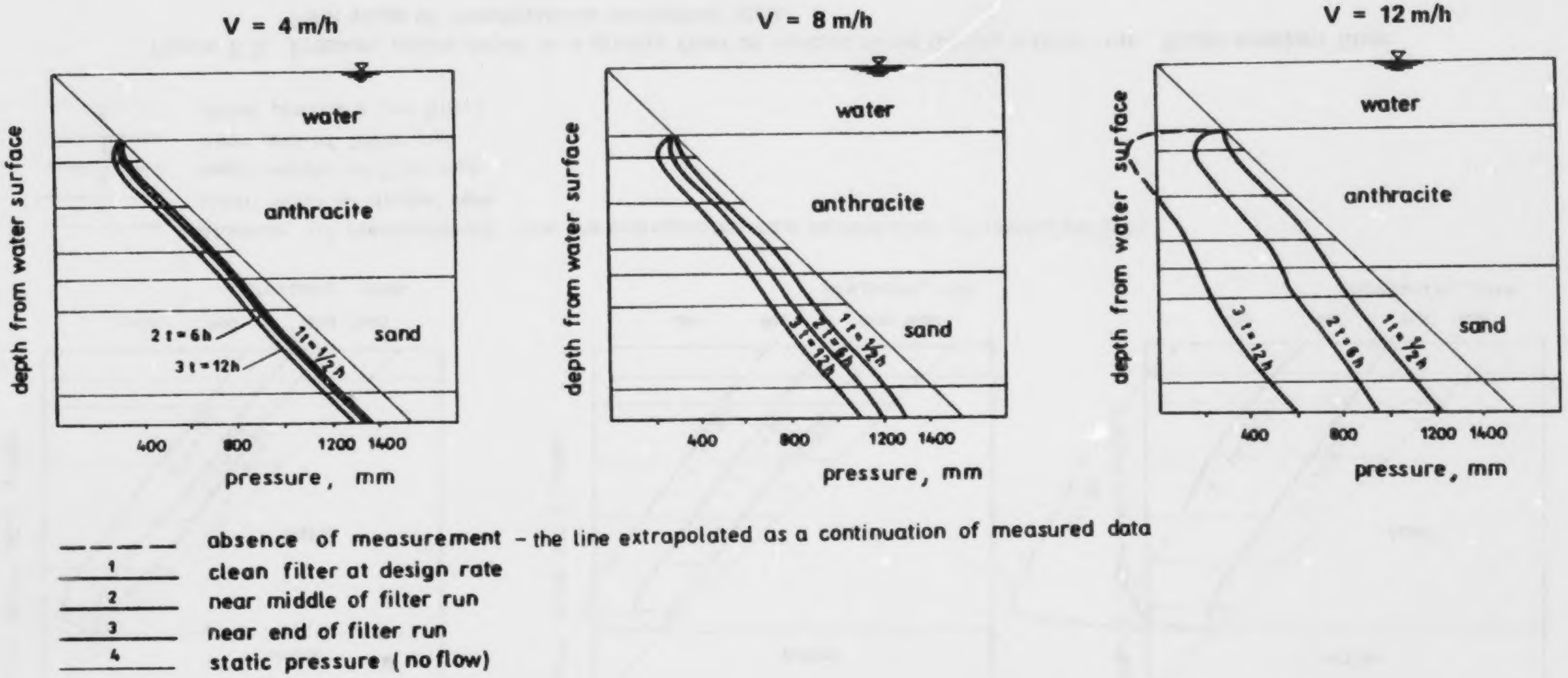
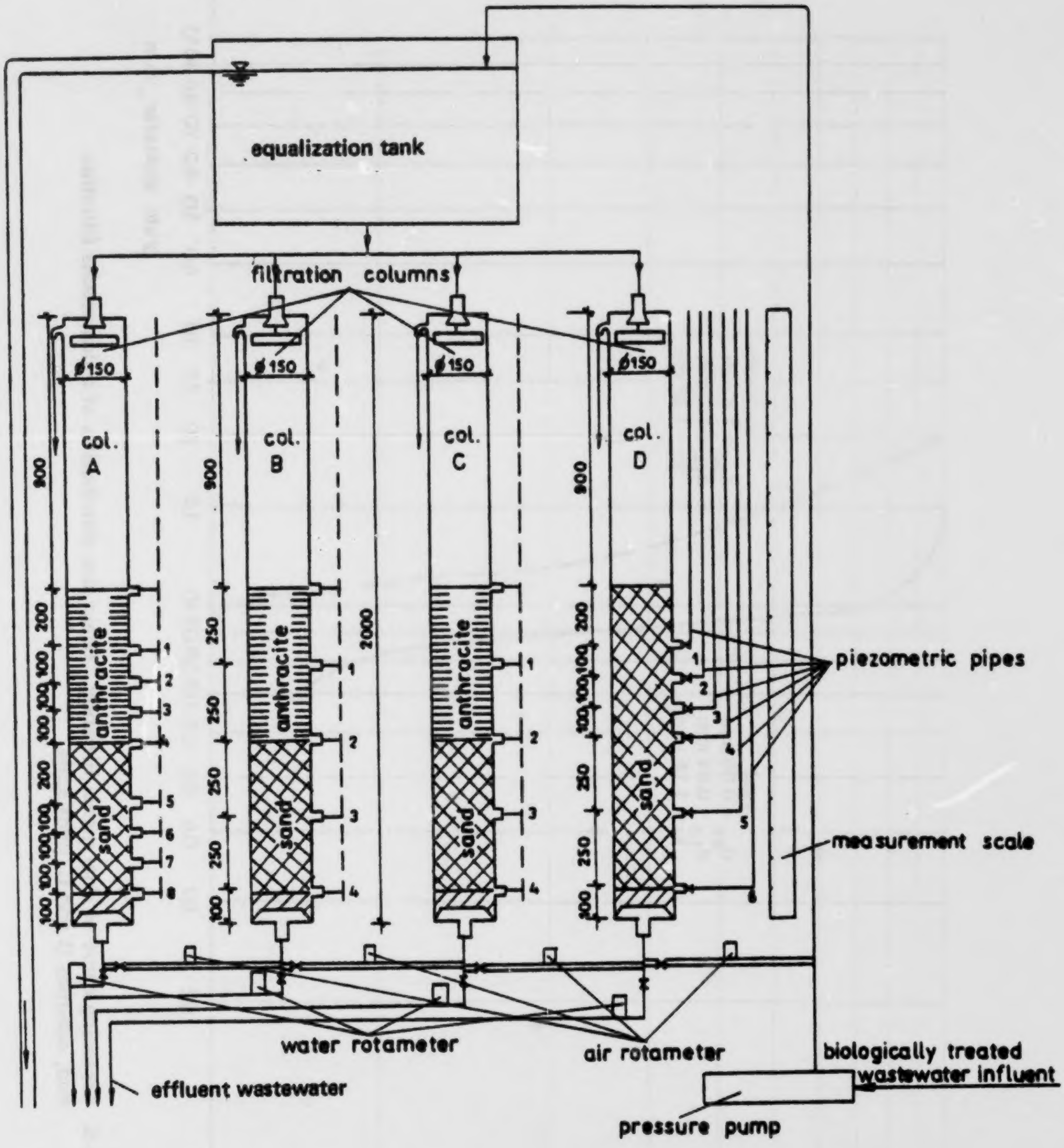


Figure 6-4. Pressure versus depth in a gravity filter at various times during a filter run. Dual media filter. First stage of investigations laboratory scale.


equalization tank
filtration columns
ø150
ø150
ø150
ø150
col. A
col. B
col. C
col. D
900
2000
anthracite
sand
piezometric pipes
measurement scale
water rotameter
air rotameter
biologically treated wastewater influent
effluent wastewater
pressure pump

Note: In series I, II, and V, only one column was working (table 6-3)

Figure 6-5. Scheme of apparatus applied for pilot plant wastewater filtration process.

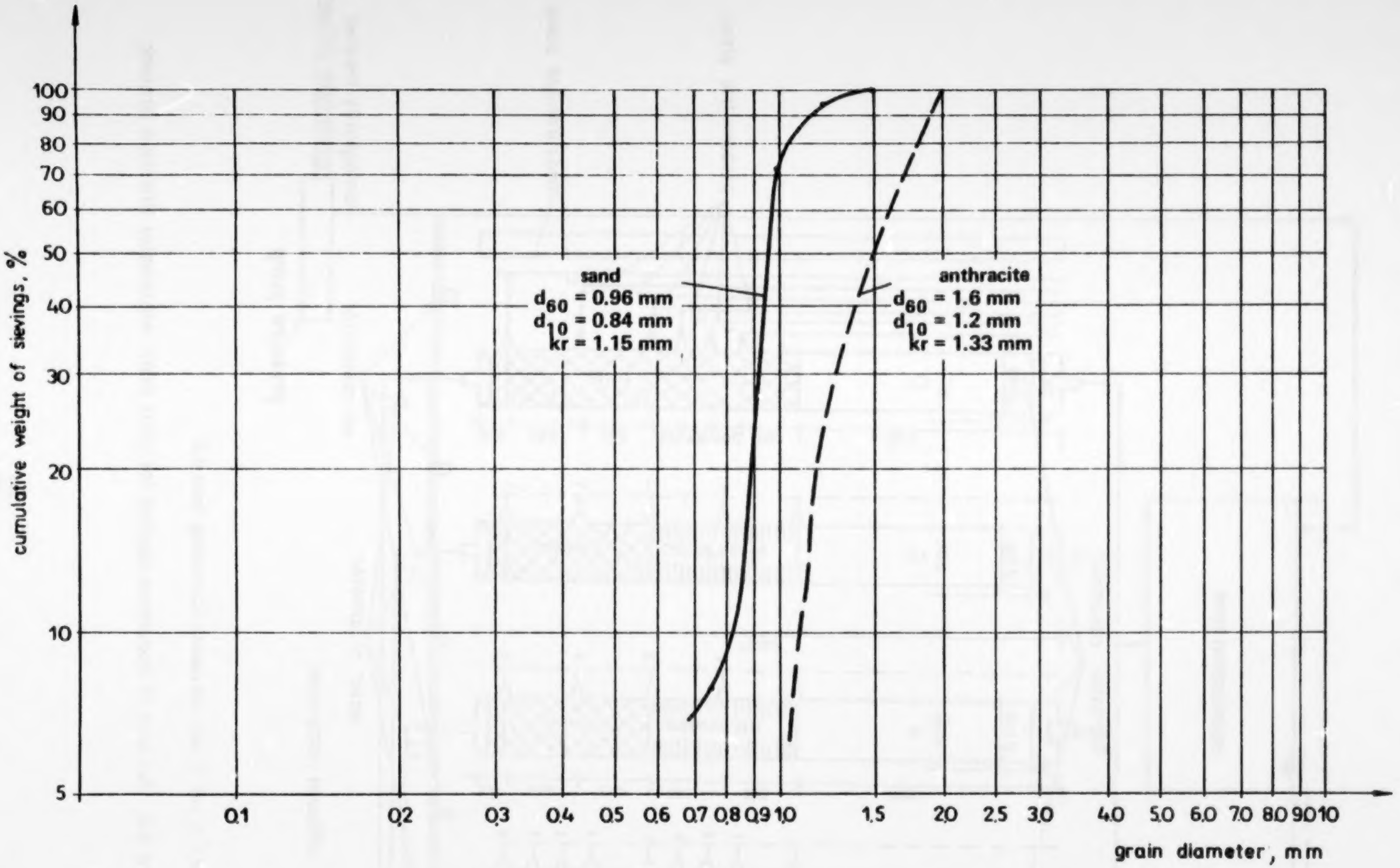


Figure 6-6. Screening curve of dual media filtration. Grain size distribution of a dual-media filtration bed, columns B and C, pilot scale.

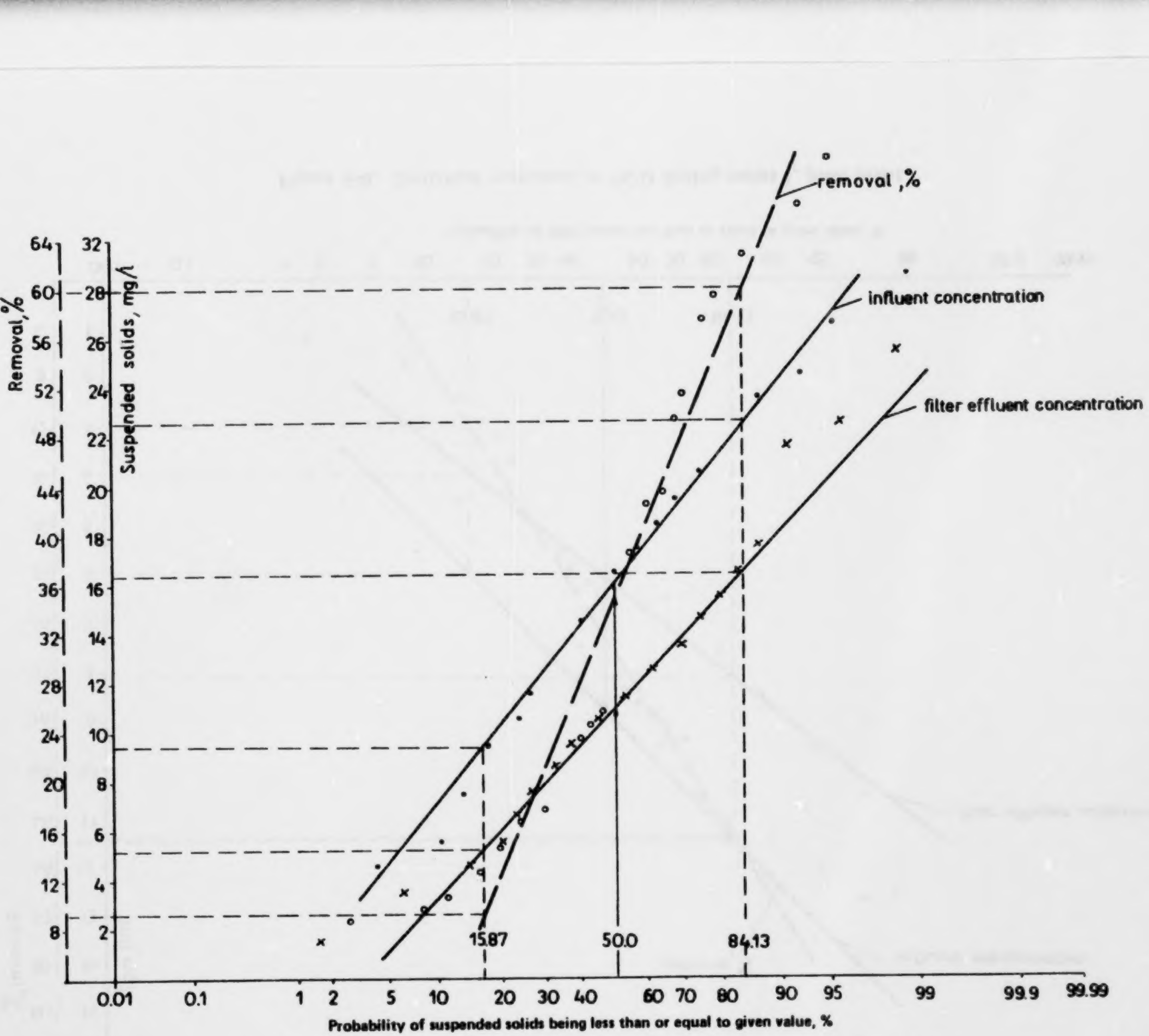


Figure 6-7. Statistical variations in suspended solids during series I, pilot plant.

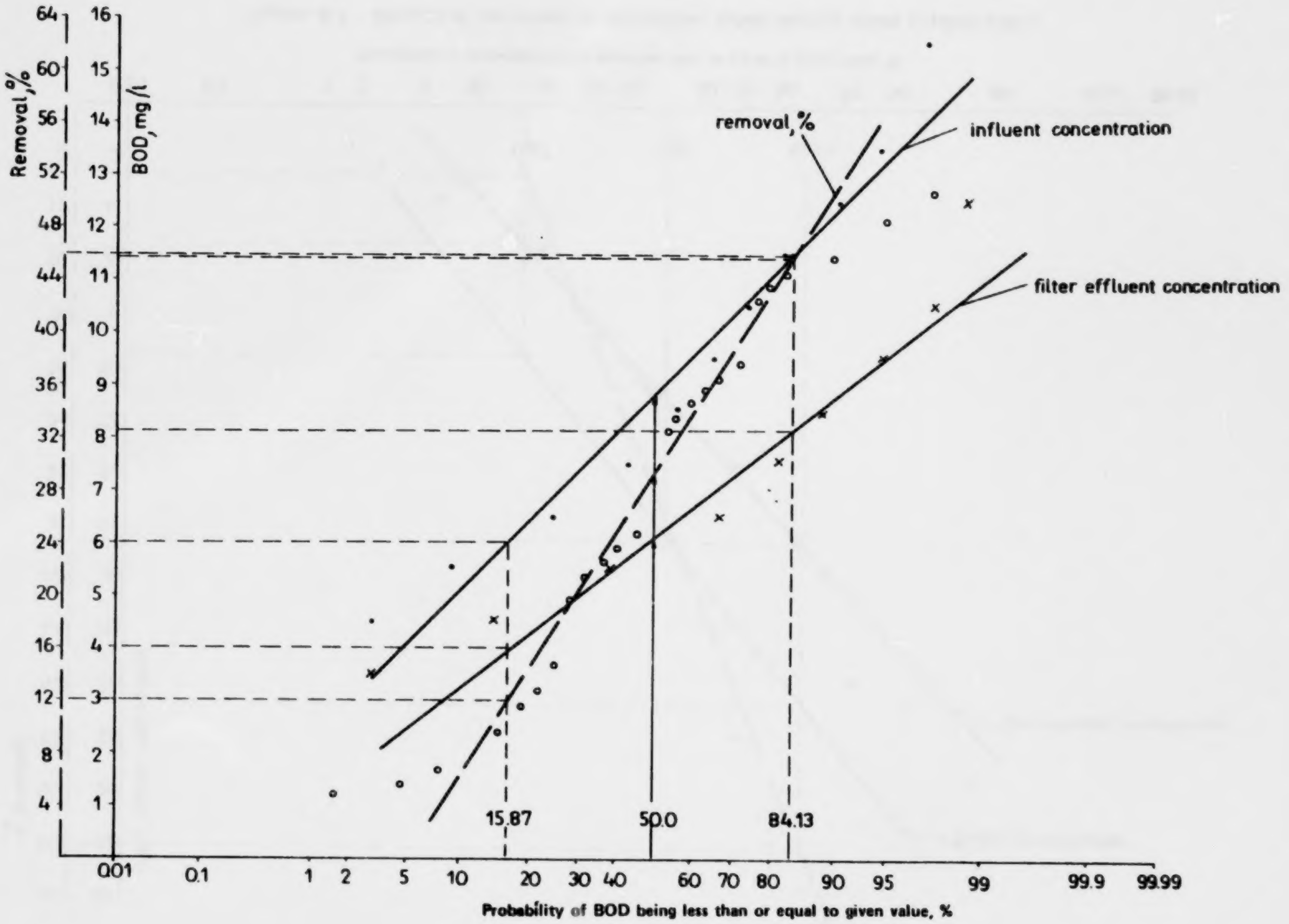


Figure 6-8. Statistical variations in BOD during series I, pilot plant.

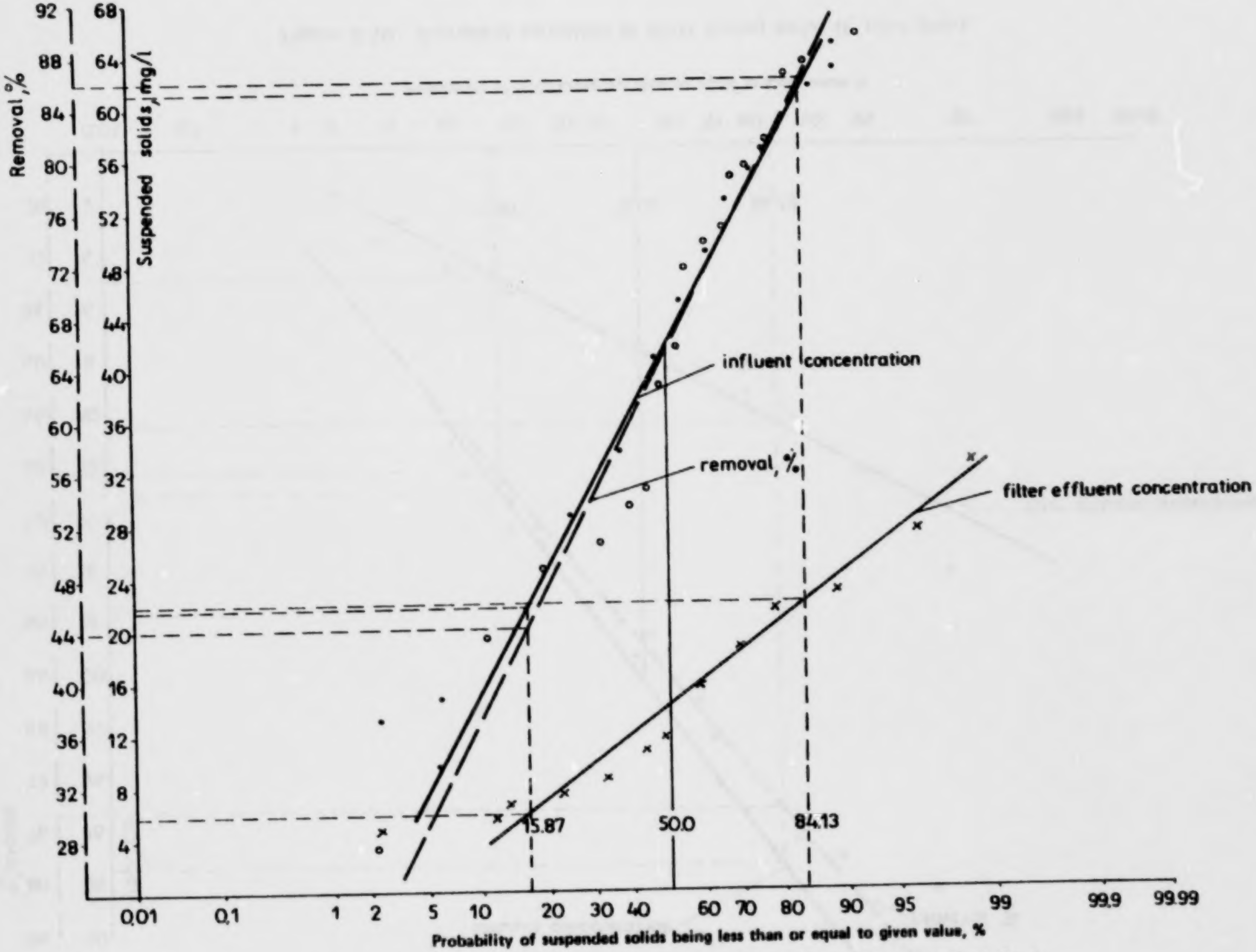


Figure 6-9. Statistical variations in suspended solids during series II, pilot plant.

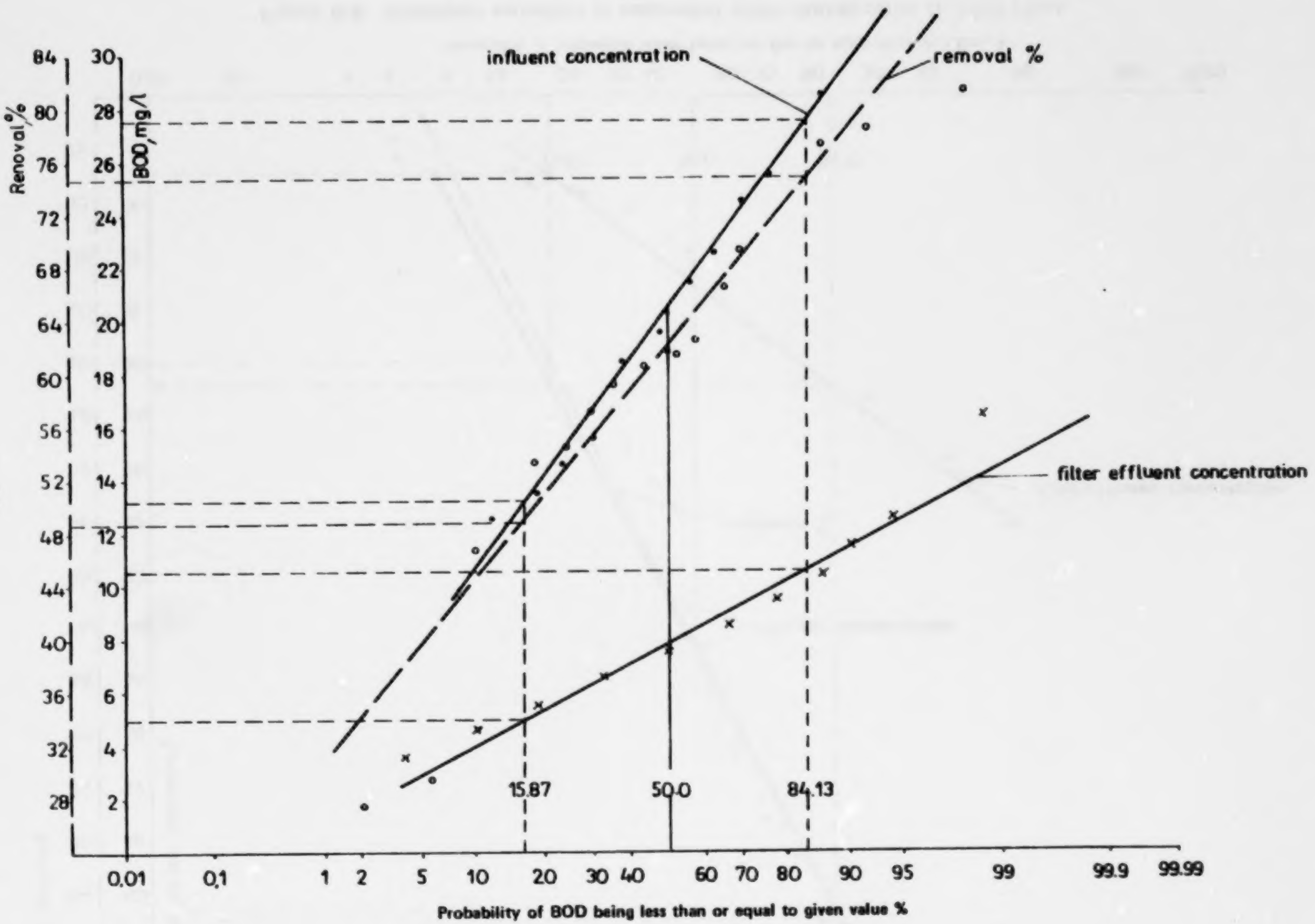


Figure 6-10. Statistical variations in BOD during series II, pilot plant.

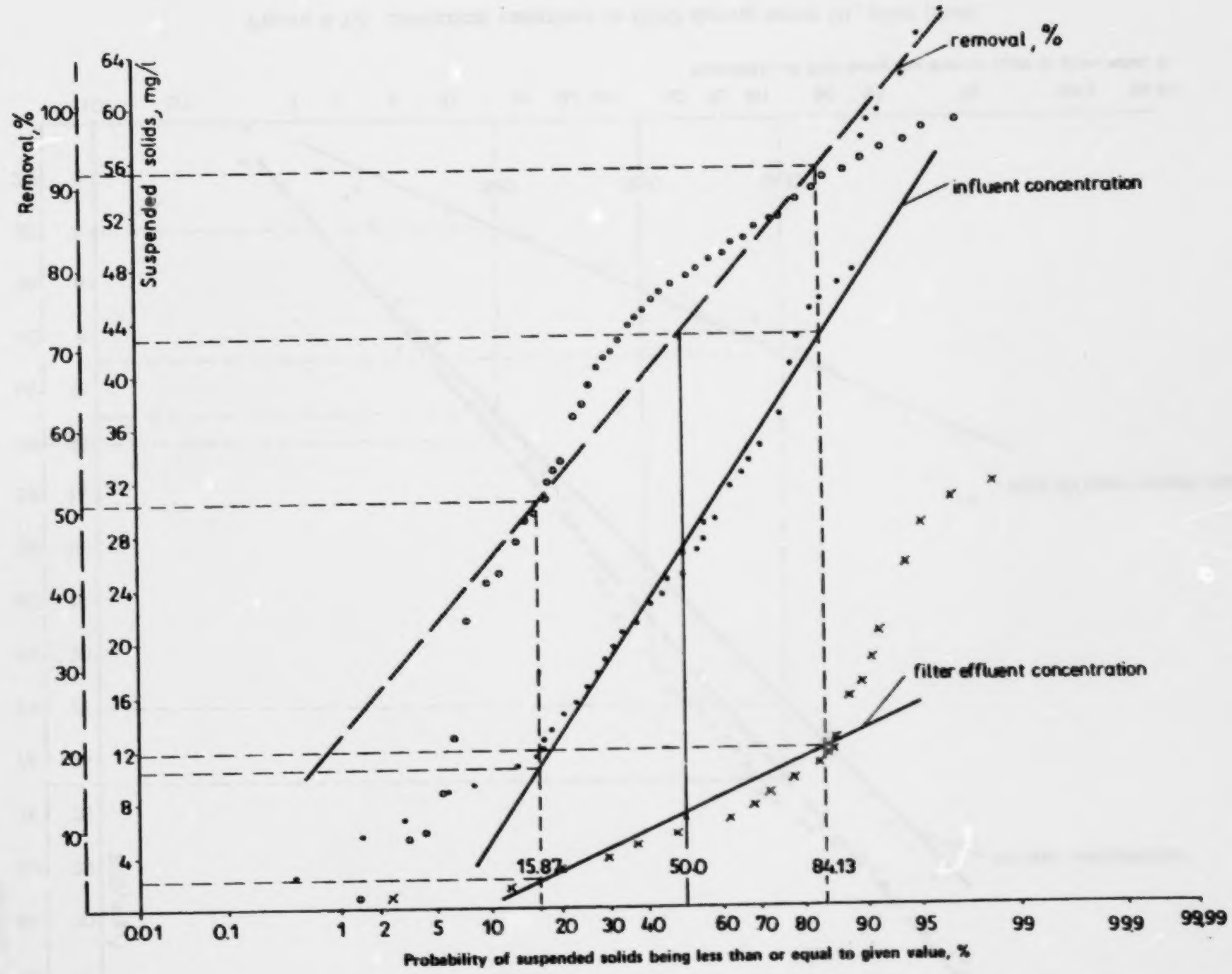


Figure 6-11. Statistical variations in suspended solids during series III, pilot plant.

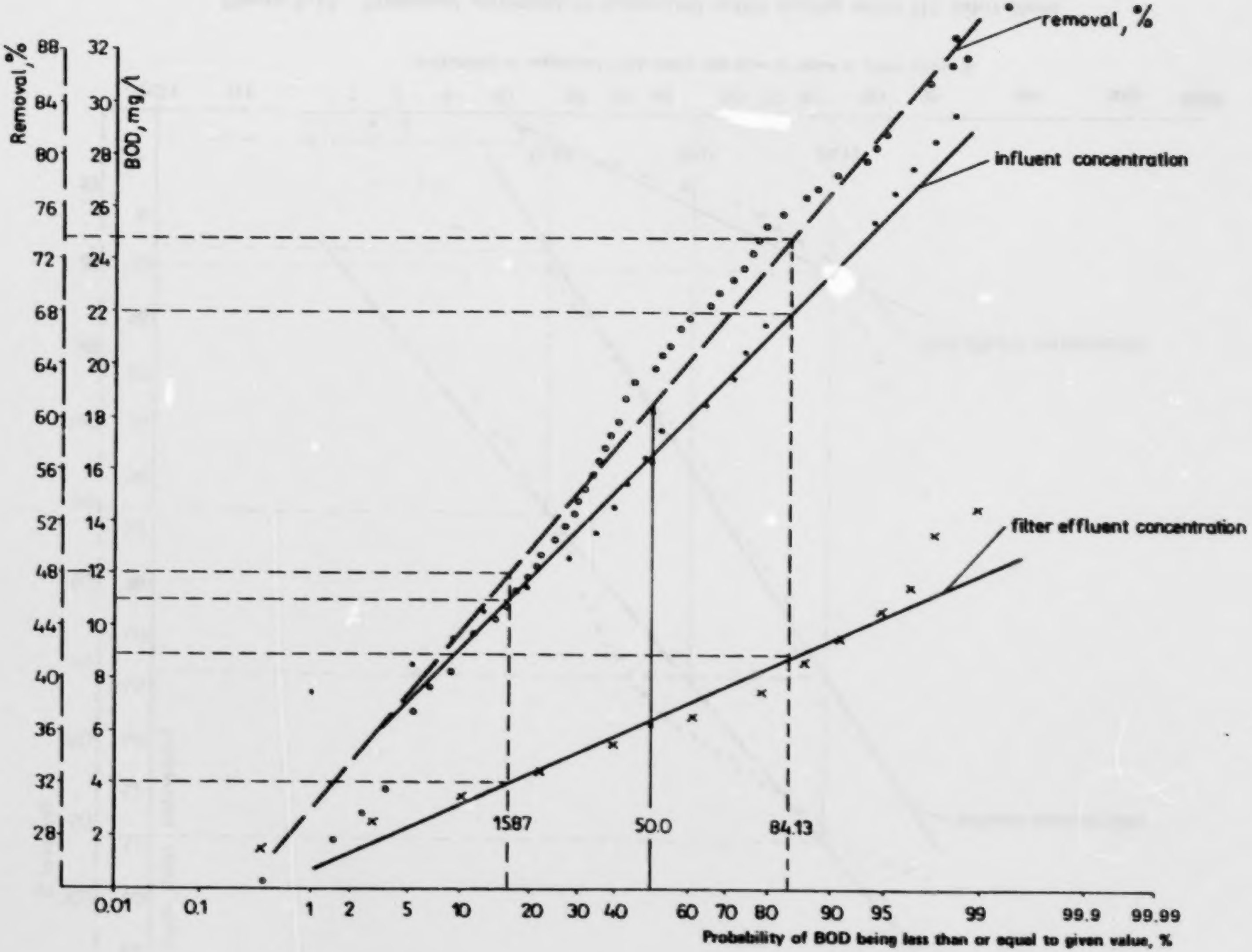


Figure 6-12. Statistical variations in BOD during series III, pilot plant.

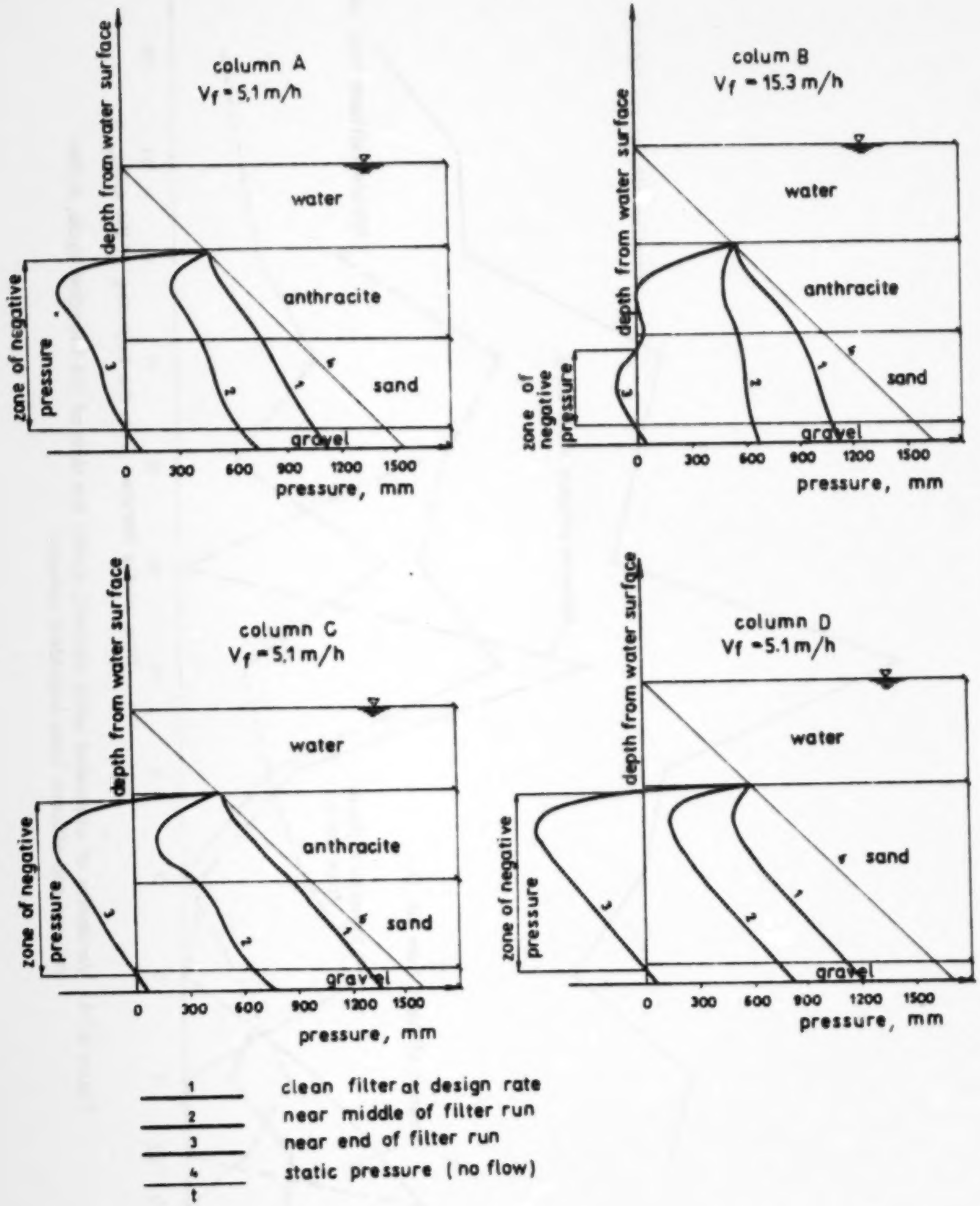


Figure 6-13. Pressure versus depth in a gravity filter at various times during a filter run. Second stage of investigation, pilot plant.

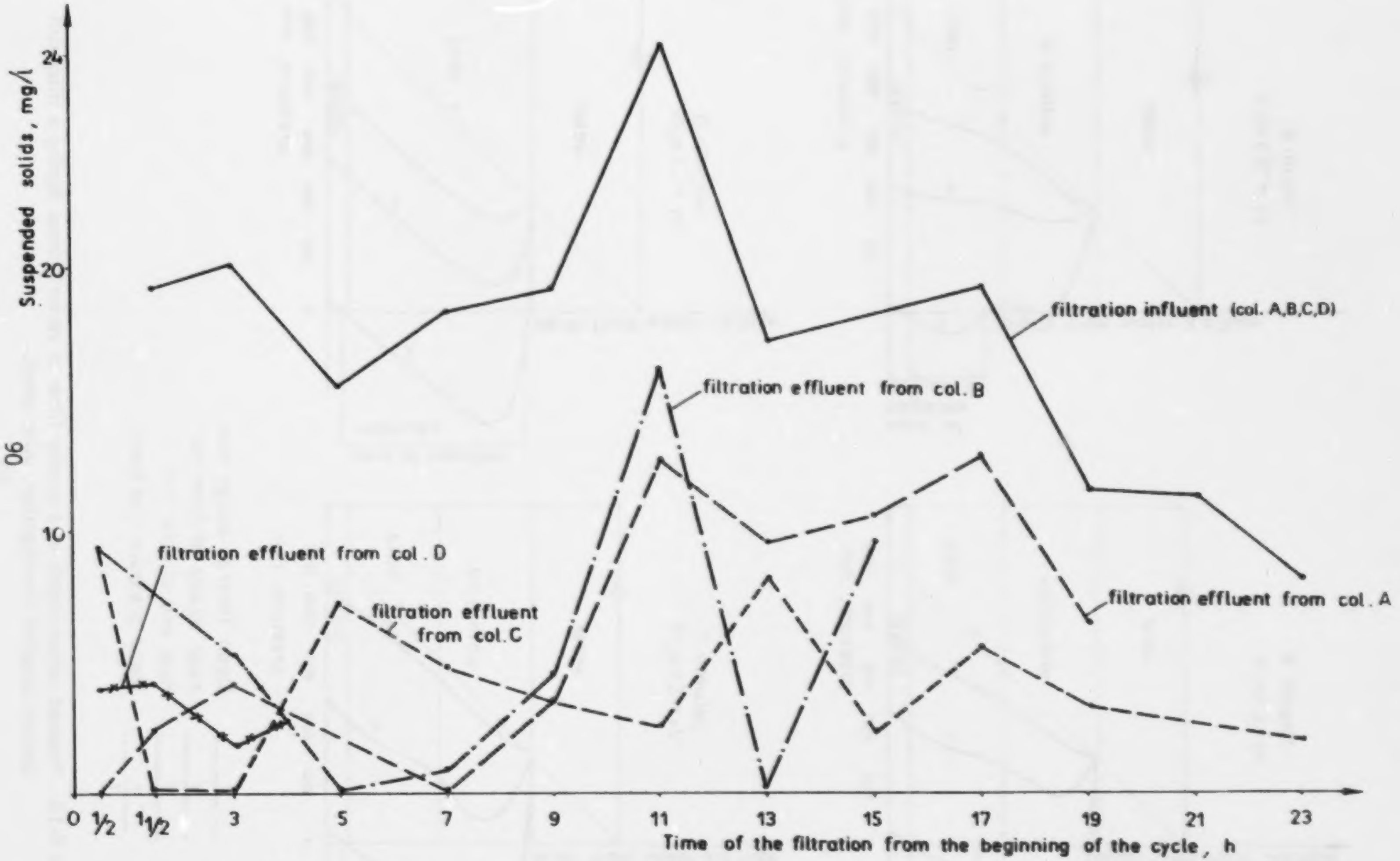


Figure 6-14. Variability of suspended solids content, during the time of the filtration cycle, in the influent and effluent from individual columns.

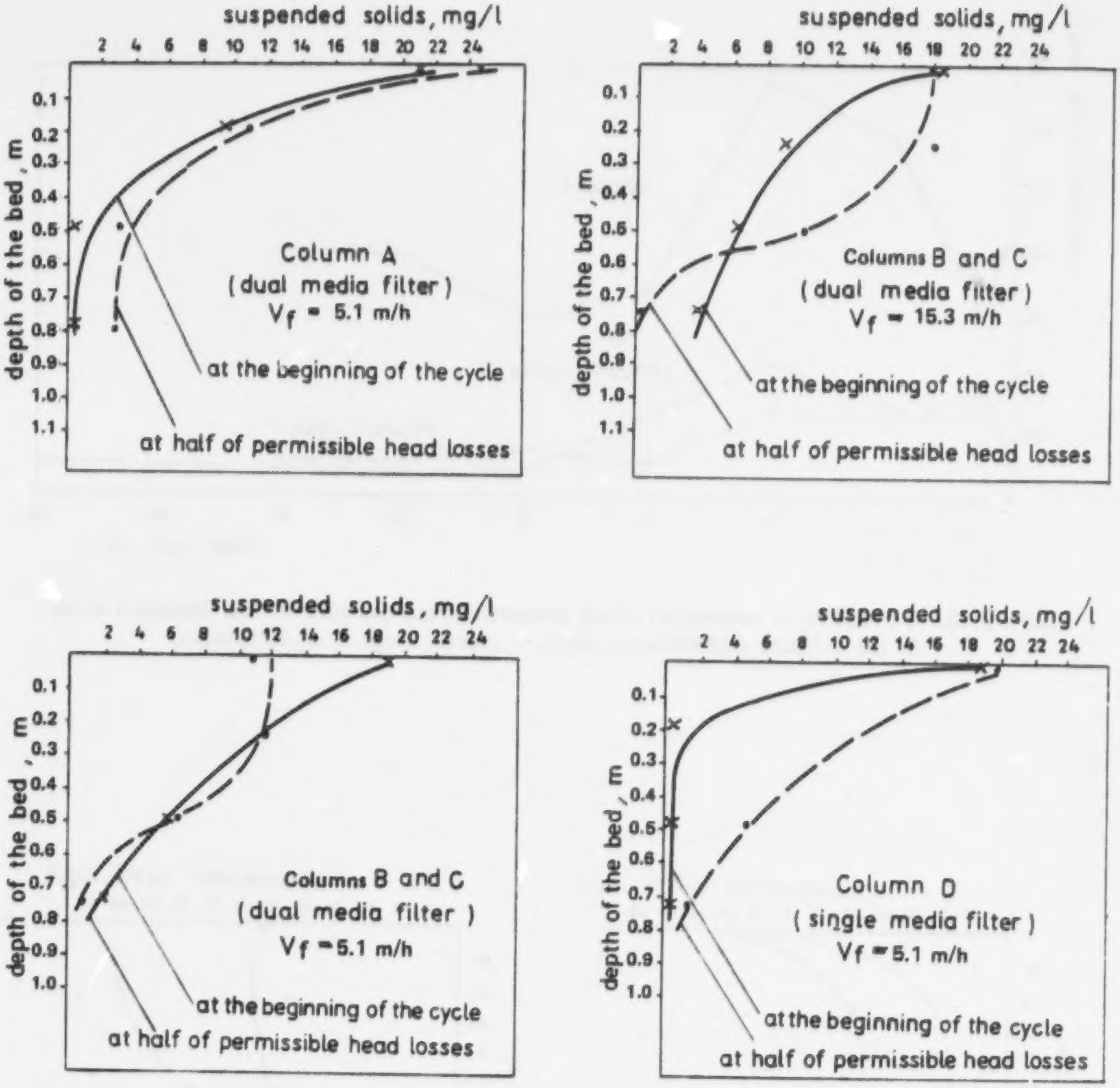


Figure 6-15. Suspended solids concentration in wastewater at various depths of the filtration bed during the filter run, pilot plant, series IV.

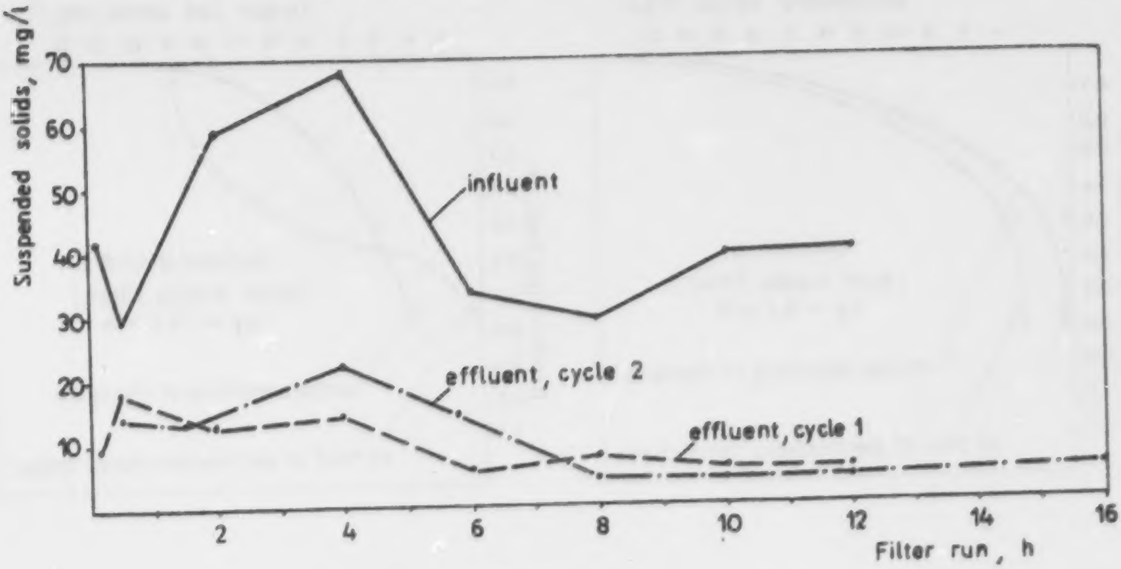


Figure 6-16. Variability of suspended solids content during the time of the filtration cycle in the influent and effluent, series v, second stage of investigation.

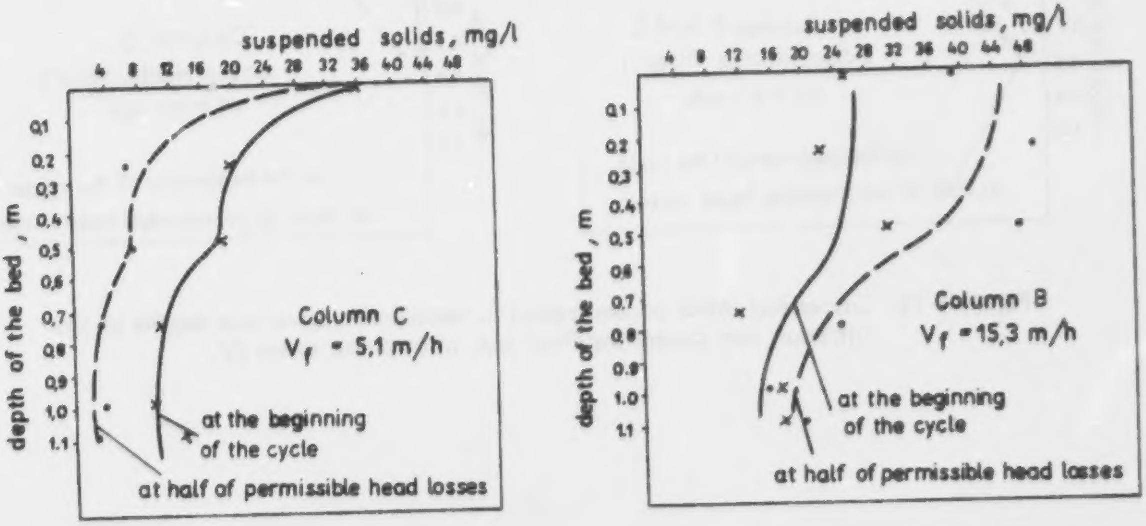


Figure 6-17. Suspended solids concentration in wastewater at various depths of the filtration bed during the filter run, pilot plant, series V.

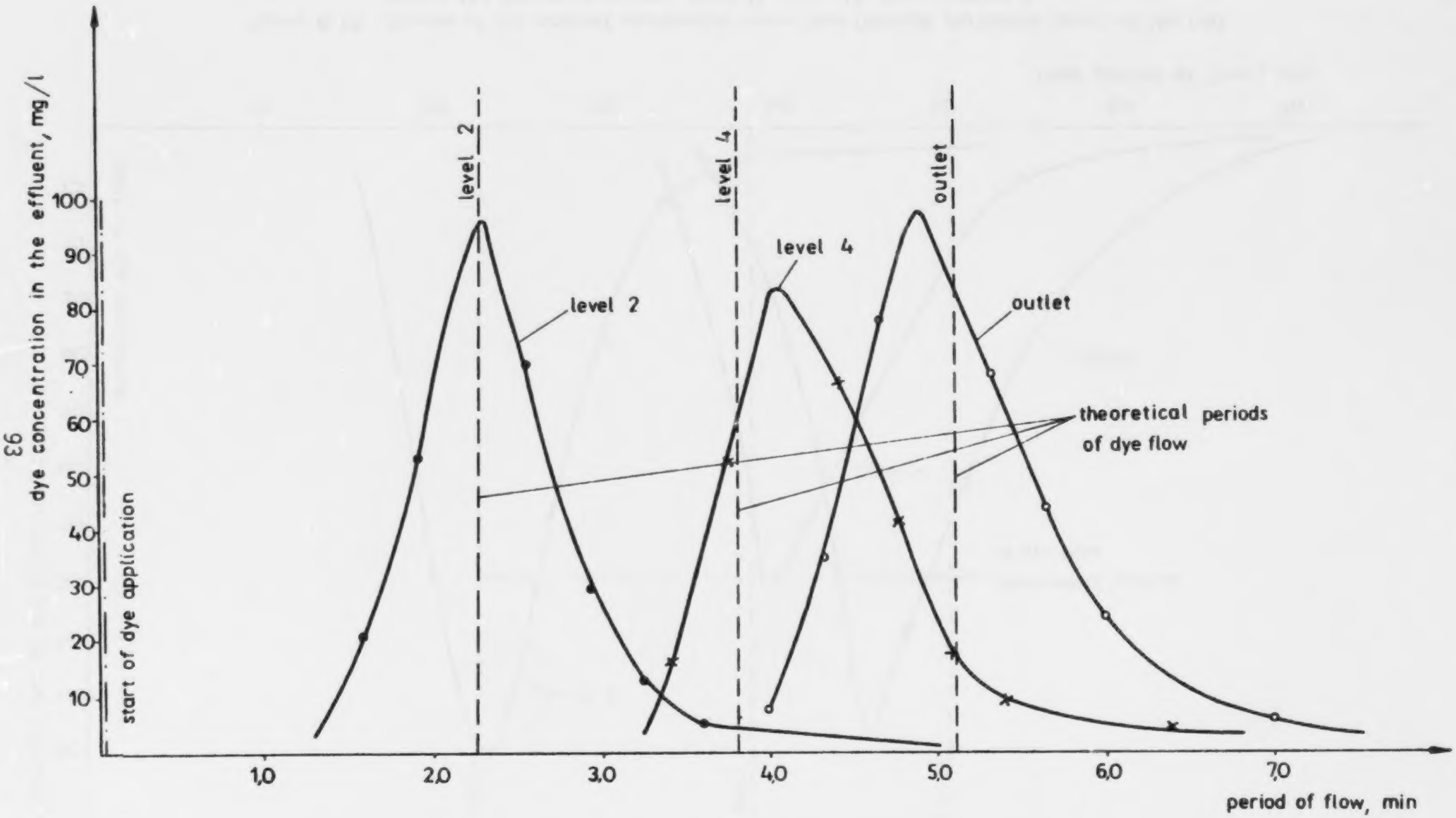


Figure 6-18. Course of the colored wastewater wave flow through particular layers of the bed during the filtration process, stage II, series V, measurement 1.

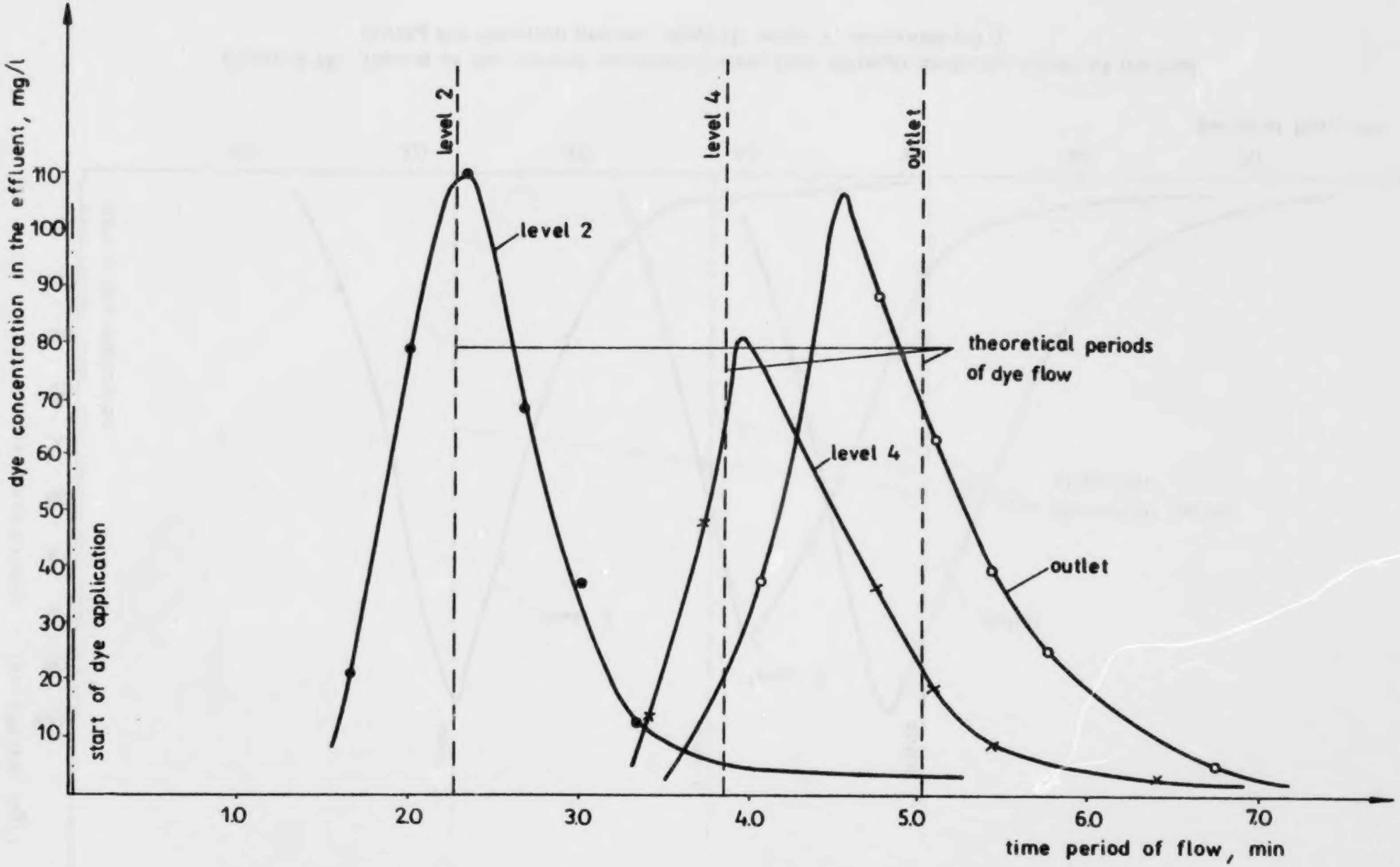


Figure 6-19. Course of the colored wastewater wave flow through particular layers of the bed during the filtration process, stage II, series V, measurement 2.

Table 6-1. Characteristics of filtration beds applied to investigations on laboratory scale, stage I

Filter type	Supporting layer		Filter media			
	Kind and height, m	Granulation, mm	Kind and height, m	Granulation, mm	Kind and height, m	Granulation, mm
A	gravel	8 to 4	sand	d_{10}=1.0	-	-
single medium filter	0.13 m	4 to 2	1 m	d_{60}=1.5	-	-
				Kr =1.5		
B	gravel	8 to 4	sand	d_{10}=0.7	anthracite	d_{10}=2
dual medium filter	0.13 m	4 to 2	0.51	d_{60}=0.8	0.58 m	d_{60}=2.6
				K_r=1.15		K_r= 1.3

Table 6-2. Effectiveness of the laboratory scale filtration process performed in the first stage of investigations

Test no.	Filter run	Rate of filtration, m^3m^2h	Time of sampling from the beginning of filter cycle, h	Amount of filtered wastewater, l/time period	Filter bed	Pressure losses, mm H_2O	Total suspended solids							
							before filtration		after filtration		concentration removal		removal %	
							total, mg/l	volatile, mg/l	total, mg/l	volatile, mg/l	total, mg/l	volatile, mg/l	total, %	volatile, %
1	12	4	0	0	A	-	56.4	36.0						
			0.5	5	single	225			9.4	1.2	47	34.8	83.3	96.7
			6	59	medium	370			8.4	1.0	48	35.0	85.1	97.2
			12	118		560			7.4	0.2	49	35.8	86.9	99.5
2	12	4	0	0	B	-	32.8	8.8						
			0.5	5	dual	170			10.5	2.5	22.3	6.3	68	71.6
			6	59	media	180			10.2	2.4	22.5	6.4	68.6	72.7
			12	118		210			8.9	2.1	23.9	6.7	72.9	76.1
3	12	8	0	0	A	-	22.8	1.6						
			0.5	10	single	200			9.8	1.2	13.0	0.4	57.0	25.0
			6	120	medium	430			7.4	1.0	15.4	0.6	67.5	37.5
			12	236		690			4.8	0.6	18.0	1.0	78.9	62.5
4	12	8	0	0	B	-	50.0	27.6						
			0.5	10	dual	220			10.8	3.8	39.2	23.6	78.4	86.2
			6	118	media	320			9.2	2.6	40.8	25.0	81.6	90.6
			12	236		420			9.8	1.2	40.2	26.4	80.4	95.6

Table 6-2 (con.)

Test no.	Filter run	Rate of filtration, m^3/m^2h	Time of sampling from the beginning of filter cycle, h	Amount of filtered wastewater, l/time period	Filter bed	Pressure losses, mm H_2O	Total suspended solids							
							before filtration		after filtration		concentration removal		removal %	
							total, mg/l	volatile, mg/l	total, mg/l	volatile, mg/l	total, mg/l	volatile, mg/l	total, %	volatile, %
5	7	12	0	0	A	-	3.4	-						
			0.5	15	single	390			1.7	-	1.7	-	50	-
			3.5	103	medium	840			1.0	-	2.4	-	70.6	-
			7	207		1,300			0.7	-	2.7	-	79.4	-
6	12	12	120	0	B	-	56.4	42.0						
			0.5	15	dual	305			27.0	20.4	29.4	21.6	52.1	51.4
			6	127	media	570			19.4	14.2	37.0	27.8	65.6	66.2
			12	354		945			15.4	10.4	41.0	31.6	72.7	

Table 6-2 (con.)

	Dissolved solids				BOD_5				Permanganate COD				Color			
Test no.	Before filtration, mg/l	After filtration, mg/l	Concentration removed, mg/l	Removal, %	Before filtration, mg O_2/l	After filtration, mg O_2/l	Concentration removed, mg O_2/l	Removal, %	Before filtration, mg O_2/l	After filtration mg O_2/l	Concentration removed, mg O_2/l	Removal, %	Filter influent, mg O_2/l	Filter effluent, mg O_2/l	Removal, mg O_2/l	Removal, %
1	1,040				50				29.0							
		1,034	6	0.6		26	24	48		18.5	10.5	36.2				
		1,017	23	2.2		20	30	60		16.5	12.5	43.1				
		1,017	23	2.2		18	32	64		11.0	18.0	62.1				
2	975				28				22.0							
		831	144	14.8		19	9	32		18.5	3.5	15.9				
		801	174	17.9		18	10	35.7		18.0	4.0	18.2				
		772	203	20.8		15	13	46		17.5	4.5	20.5				
3	882				27				22.5							
		876	6	0.7		20	7	25.9		28.0	4.5	20				
		831	51	5.8		17	10	37		17.5	5.0	22.2				
		830	22	2.5		15	12	44.4		16.5	6.0	26.7				
4	927				22				18.5							
		907	20	2.2		10	12	54.5		15.5	3.0	16.2				
		896	31	3.4		6	16	72.7		14.5	4.0	21.6				
		903	24	2.6		8	14	63.6		13.5	5.0	27.0				

Table 6-2 (con.)

	Dissolved solids				BOD$_5$				Permanganate COD				Color			
Test no.	Before filtration, mg/l	After filtration, mg/l	Concentration removed, mg/l	Removal, %	Before filtration, mg O_2/l	After filtration, mg O_2/l	Concentration removed, mg O_2/l	Removal, %	Before filtration, mg O_2/l	After filtration, mg O_2/l	Concentration removed, mg O_2/l	Removal, %	Filter influent, mg O_2/l	Filter effluent, mg O_2/l	Removal, mg O_2/l	Removal, %
5	301				20				9.0				20			
		344	-	-		12.5	7.5	37.5		5.5	3.5	38.9		20	-	-
		303	-	-		11.0	9	45.0		5.0	4.0	44.4		20	-	-
		330	-	-		10.0	10	50.0		4.5	4.5	50.0		20	-	-
6	852				27				23.5				50			
		836	16	1.9		12	15	55.6		22	1.5	6.4		50	-	-
		849	3	0.3		10	17	63		21.5	2.0	8.5		60	-	-
		752	100	11.7		7	20	74.1		21.0	2.5	10.6		70	-	-

Table 6-3. Characteristics of the filtration beds used for pilot plant investigations (IInd stage)

Series	Determination of the filtration column	Supporting layer		Filtration layer		Rate of filtration, $m^3/m^2/h$	Average cycle length corresponding to head losses (h)
		Kind of material, m	Granulation, mm	Kind of material and height, m	Granulation, mm		
1	2	3	4	5	6	7	8
I	-	gravel 0.10	2-10 mm	sand 1.00	0.5-0.75	5.3	12
II	-	gravel 0.10	2-10 mm	sand 1.00	0.5-0.75	5.3	23
III	-	gravel 0.10	2-10 mm	sand 0.5	0.4-0.75	5.1	23
				anthracite 0.5	0.5-0.75		
IV	A	gravel 0.10	2-10 mm	sand 0.5	0.4-0.75	5.1	19.5
				anthracite 0.5	0.4-0.75		
	B	gravel 0.10	2-10 mm	sand 0.5	0.75-1.5	15.3	14.0
				anthracite 0.5	1.5-2.0		
	C	gravel 0.10	2-10 mm	sand 0.5	0.75-1.5	5.1	34.0
				anthracite 0.5	1.5-2.0		
	D	gravel 0.10	2-10 mm	sand 1.0	0.5-1.5	5.1	5.5
V	B or C	gravel 0.10	2-10 mm	sand 0.5	0.75-1.5	5.1	20
				anthracite 0.5	1.5-2.0	15.0	

Table 6-4. Filtration bed values for column B

	Anthracite	Sand
Porosity, in %	38.0	27.5
Bulk density, in g/cm^3	0.97	1.78
Specific gravity, in g/cm^3	1.56	2.45

Table 6-5. Effects of contaminant removal during filtration in pilot scale investigations, series I, stage II

Date/indicator		74 r 2/12	2/13	2/14	2/15	2/16	2/19	2/20	2/21	2/22	2/23	2/26	2/27
Suspended solids concentration													
influent	mg/l	17.8	21.4	13.6	24.2	16.0	4.2	20.8	26.2	16.6	19.8	18.0	18.0
effluent	mg/l	14.6	13.2	5.1	21.8	6.5	1.2	12.8	7.2	12.4	15.2	10.1	8.8
removal	%	18.0	38.3	62.3	9.9	59.4	71.4	38.5	72.5	25.3	23.2	43.9	51.1
BOD_5 concentration													
influent	mg O_2/l	10.0	8.8	7.5	11.7	11.5	18.0	15.0	6.6	6.0	5.5	12.1	6.6
effluent	mg O_2/l	6.4	5.5	5.1	5.8	8.8	9.2	9.7	5.0	5.7	4.3	7.7	6.1
removal	%	36.0	37.5	32.0	50.4	23.5	48.9	35.3	24.2	5.0	21.8	36.4	7.6
COD concentration													
influent	mg O_2/l	79.2	36.8	36.0	56.8	94.8	74.9	62.2	85.9	85.9	83.5	40.0	-
effluent	mg O_2/l	12.0	28.0	32.8	46.4	85.7	20.0	40.8	81.6	81.6	80.0	16.0	-
removal	%	84.8	23.9	8.9	18.3	9.6	73.3	34.4	5.0	5.0	4.2	60.0	-
Oxygen permanganate COD													
influent	mg O_2/l	18.0	21.0	19.0	20.0	17.5	17.5	20.5	18.5	17.0	17.5	14.5	13.5
effluent	mg O_2/l	6.5	9.0	13.0	12.0	13.0	12.0	14.0	13.0	14.0	13.0	12.0	11.0
removal	%	63.9	57.1	31.6	40.0	25.7	31.4	31.7	29.7	17.6	25.7	17.2	18.5
Color													
influent	mg Pt/l	40	60	40	60	60	60	40	80	60	45	35	45
effluent	mg Pt/l	25	40	40	40	40	40	35	40	40	35	35	35
removal	%	37.5	33.3	0.0	33.3	33.3	33.3	14.3	50	33.3	22.2	0.0	22.2
Anionic detergents													
influent	mg/l	3.82	-	-	-	4.00	-	-	3.25	-	-	3.02	-
effluent	mg/l	1.42	-	-	-	2.59	-	-	1.51	-	-	2.41	-
removal	%	62.8	-	-	-	35.3	-	-	53.5	-	-	20.2	-

Table 6-5 (con.)

Date/indicator		2/28	3/01	3/02	3/03	3/05	3/06	3/07	3/08	3/08	3/10	3/12
Suspended solids concentration												
influent	mg/l	9.8	12.4	20.4	10.6	22.7	12.4	14.2	28.0	24.4	21.6	18.6
effluent	mg/l	9.0	11.4	17.0	11.6	8.6	13.6	4.8	22.8	12.4	4.4	16.0
removal	%	8.2	8.1	16.7	-	62.1	-	66.2	18.6	49.2	62.1	14.0
BOD_5 concentration												
influent	mg O_2/l	6.5	4.5	6.7	6.8	7.7	4.1	7.0	7.0	8.1	5.7	12.5
effluent	mg O_2/l	5.0	4.2	5.1	4.8	6.6	3.9	4.0	5.4	6.5	6.1	12.6
removal	%	23.1	6.7	23.9	29.4	14.3	4.9	42.9	22.9	19.8	-	-
COD concentration												
influent	mg O_2/l	-	30.4	51.2	27.9	82.0	48.0	99.0	90.0	81.5	56.0	38.0
effluent	mg O_2/l	-	25.6	32.7	23.1	56.8	48.0	79.2	69.0	56.0	48.0	38.0
removal	%	-	15.8	36.1	17.2	30.7	-	20.0	23.3	31.3	14.3	34.5
Oxygen permanganate COD												
influent	mg O_2/l	17.0	13.5	16.5	17.0	18.0	12.0	13.5	15.0	16.0	13.5	12.0
effluent	mg O_2/l	13.0	12.7	13.0	15.0	12.0	12.0	12.0	14.5	14.0	13.2	10.0
removal	%	23.5	5.9	21.2	11.8	33.3	-	11.1	3.3	12.5	2.2	16.7
Color												
influent	mg Pt/l	60	60	60	80	70	55	60	60	50	60	40
effluent	mg Pt/l	40	40	60	80	70	45	50	60	40	50	40
removal	%	33.3	33.3	0.0	0.0	0.0	18.2	16.7	0.0	20.0	16.7	0.0
Anionic detergents												
influent	mg/l	-	3.02	-	-	3.58	-	-	-	2.78	-	-
effluent	mg/l	-	2.41	-	-	2.78	-	-	-	2.41	-	-
removal	%	-	20.2	-	-	22.3	-	-	-	13.3	-	-

Table 6-5 (con.)

Date/indicator		3/13	3/14	3/15	3/16	3/17	3/19	3/20	3/21	3/22	3/23	Average in series I
Suspended solids concentration												
influent	mg/l	16.8	5.6	4.0	9.4	23.5	7.8	14.4	20.8	14.4	4.0	15.8
effluent	mg/l	10.8	3.2	3.3	21.6	10.0	7.0	25.8	15.8	12.0	3.5	11.3
removal	%	35.7	42.9	17.5	-	57.4	10.3	0	24.0	16.7	12.5	28.4
BOD_5 concentration												
influent	mg O_2/l	6.5	7.5	9.0	11.7	9.8	11.0	10.0	9.2	8.6	6.7	8.7
effluent	mg O_2/l	5.9	6.6	8.0	7.7	6.5	6.0	5.7	5.0	4.8	3.7	6.2
removal	%	9.2	12.0	11.1	34.2	33.7	45.5	43.0	45.7	44.2	44.8	28.7
COD concentration												
influent	mg O_2/l	56.0	56.0	120.8	71.2	91.2	140.2	101.0	156.0	64.0	58.2	73.4
effluent	mg O_2/l	24.0	40.0	198.5	56.3	90.0	92.0	98.2	148.0	61.6	51.7	60.1
removal	%	57.1	28.6	-	20.9	1.3	34.4	2.8	5.1	3.0	11.2	18.1
Oxygen permanganate COD												
influent	mg O_2/l	10.5	14.0	22.5	19.5	10.5	16.0	14.5	20.0	20.0	13.5	16.3
effluent	mg O_2/l	7.7	12.0	17.2	14.0	10.5	13.5	13.5	17.5	15.5	12.5	12.6
removal	%	26.7	14.3	23.6	28.2	-	15.6	6.9	12.5	22.5	7.4	22.6
Color												
influent	mg Pt/l	40	50	50	60	60	60	60	80	60	50	56.1
effluent	mg Pt/l	30	40	40	50	50	50	50	50	50	50	44.8
removal	%	25.0	20.0	20.0	16.7	16.7	16.7	16.7	37.5	16.7	0.0	20.1
Anionic detergents												
influent	mg/l	3.58	-	4.01	-	-	3.40	-	4.81	-	-	3.57
effluent	mg/l	2.78	-	3.30	-	-	3.02	-	4.20	-	-	2.62
removal	%	22.3	-	17.7	-	-	11.2	-	12.7	-	-	26.6

Table 6-6. Effects of contaminant removal during filtration in pilot scale investigations, series II, stage II

Date/indicator		4/26	4/27	4/27	4/30	5/01	5/03	5/04	5/04	5/07	5/08	5/09	5/10	5/10
Suspended solids concentration														
influent	mg/l	40.4	33.6	54.8	53.2	28.0	64.6	63.4	58.2	40.4	13.4	45.2	49.4	32.8
effluent	mg/l	39.4	22.2	32.4	27.2	6.0	8.2	21.6	6.0	8.4	6.2	11.8	22.6	18.8
removal	%	1.0	33.0	50.0	48.0	78.0	87.0	65.0	89.0	79.0	53.0	73.9	54.3	42.7
BOD_5														
influent	mg O_2/l	14.5	15.0	13.5	18.0	19.2	25.5	22.0	19.5	21.7	12.6	24.0	25.0	22.9
effluent	mg O_2/l	10.5	7.0	9.5	7.0	8.1	11.7	6.1	3.7	8.6	6.7	9.7	7.5	9.0
removal	%	27.6	53.3	29.6	61.1	57.8	54.1	72.3	81.0	60.4	46.8	59.6	70.0	60.7
COD														
influent	mg O_2/l	108.0	115.9	159.6	177.1	67.0	104.7	111.4	145.6	78.5	171.0	100.0	105.6	100.0
effluent	mg O_2/l	99.0	107.8	126.0	28.7	34.0	40.5	39.4	39.5	28.6	48.0	62.8	53.8	64.2
removal	%	8.3	7.0	21.0	83.8	49.3	61.3	64.6	72.9	63.6	71.9	37.2	49.1	35.8
Oxygen permanganate COD														
influent	mg O_2/l	31.0	27.0	24.5	26.5	16.5	30.5	25.0	28.0	19.5	18.0	21.5	22.5	21.5
effluent	mg O_2/l	29.5	23.0	19.5	6.0	10.0	10.5	15.0	10.0	13.5	13.5	17.0	15.5	17.5
removal	%	4.8	14.8	20.4	77.4	39.4	65.6	40.0	64.3	30.8	25.0	20.9	31.1	18.6
Color														
influent	mg Pt/l	80.0	90	80	60	40	40	60	70	40	40	50	70	80
effluent	mg Pt/l	80	90	80	20	35	30	60	40	40	40	50	70	70
removal	%	0.0	0.0	0.0	66.7	12.5	25.0	0.0	42.9	0.0	0.0	0.0	0.0	12.5
Anionic detergents														
influent	mg/l	6.25	-	-	10.0	-	9.8	-	-	4.5	-	-	4.5	-
effluent	mg/l	5.25	-	-	3.8	-	4.0	-	-	3.2	-	-	3.5	-
removal	%	16.0	-	-	62.0	0	59.2	-	-	28.9	-	-	2.2	-

Table 6-6 (con.)

Date/indicator		5/11	5/14	5/15	5/16	5/17	5/17	5/18	5/21	5/22	5/23	5/24	5/25	Average in series II
Suspended solids concentration														
influent	mg/l	49.2	56.2	67.0	62.4	14.0	114.2	115.2	21.2	28.8	28.2	16.8	37.0	47.5
effluent	mg/l	18.6	15.8	4.2	6.8	10.2	15.8	21.0	10.4	7.4	14.4	8.6	18.4	15.3
removal	%	62.2	71.9	93.7	89.1	27.1	86.2	81.8	50.9	74.3	48.9	48.8	50.3	67.8
BOD_5														
influent	mg O_2/l	12.6	35.0	36.9	27.3	18.7	33.9	28.0	10.0	18.6	22.3	10.0	14.1	20.8
effluent	mg O_2/l	5.1	16.1	12.3	6.0	7.1	7.8	6.0	5.3	5.1	8.8	3.4	4.3	7.7
removal	%	59.5	54.0	66.7	78.0	62.0	77.0	78.6	47.0	72.6	60.5	66.0	69.5	63.0
COD														
influent	mg O_2/l	121.5	162.6	166.0	189.1	70.9	188.7	90.8	57.1	92.6	145.7	95.4	81.8	120.3
effluent	mg O_2/l	60.5	59.0	65.5	82.1	56.3	75.5	75.4	44.7	45.4	82.4	63.6	50.0	61.7
removal	%	50.2	63.7	60.5	56.6	20.6	60.0	17.0	21.7	51.0	43.4	33.3	38.9	48.7
Oxygen permanganate COD														
influent	mg O_2/l	28.0	32.5	39.0	57.0	20.5	47.0	39.0	14.5	30.0	32.0	19.5	17.5	27.5
effluent	mg O_2/l	19.5	17.5	16.5	24.5	18.5	19.5	18.0	13.0	15.0	24.0	16.5	14.0	16.7
removal	%	30.4	46.2	57.7	57.0	9.8	58.5	53.8	10.3	50.0	25.0	15.4	20.0	39.3
Color														
influent	mg Pt/l	70	60	60	80	70	50	50	30	30	70	60	50	59.2
effluent	mg Pt/l	70	60	60	80	70	50	50	30	30	70	60	50	55.4
removal	%	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	6.4
Anionic detergents														
influent	mg/l	-	4.3	-	8.5	-	-	-	12.5	-	-	6.5	-	7.40
effluent	mg/l	-	3.6	-	4.4	-	-	-	6.0	-	-	6.5	-	4.47
removal	%	-	16.3	-	48.2	-	-	-	52.0	-	-	0.0	-	39.6

Table 6-7. Effectiveness of the pilot plant filtration process performed in series III, stage II

Date/indicator	8/28	8/29	8/30	9/03	9/04	9/05	9/06	9/07	9/10	9/12	9/12	9/17	9/18	9/19	9/20
Suspended solids															
influent mg/l	139.4	37.2	40.0	26.2	34.4	44.0	26.0	34.6	27.6	65.4	25.2	46.2	40.0	29.6	23.0
effluent mg/l	18.6	4.0	0.2	1.2	5.6	16.6	9.0	20.2	7.2	25.4	6.2	9.8	9.4	4.4	5.0
removal %	86.7	89.3	99.5	95.4	83.7	62.3	65.4	41.6	73.9	61.2	75.4	78.8	76.5	85.0	78.3
BOD_5															
influent mg O_2/l	18.6	8.0	21.0	26.7	15.0	15.0	23.0	32.8	21.7	40.3	25.8	21.5	18.3	20.1	11.6
effluent mg O_2/l	6.0	9.0	5.4	14.2	5.5	9.0	8.2	14.2	7.2	10.0	5.5	5.4	8.5	6.2	5.0
removal %	67.7	-	74.3	46.8	63.3	40.0	64.4	56.7	66.8	75.2	78.7	74.9	53.0	69.2	56.9
COD															
influent mg O_2/l	81.7	108.3	105.6	79.9	93.8	105.6	147.8	160.2	170.3	140.0	123.8	70.0	101.9	120.0	124.5
effluent mg O_2/l	58.9	55.1	50.0	55.2	53.1	59.5	76.8	95.0	63.1	48.0	57.1	34.0	65.4	80.0	92.5
removal %	27.9	49.1	52.6	30.9	43.4	43.6	48.1	40.7	41.2	65.7	53.8	51.4	25.0	33.3	25.8
Permanganate COD															
influent mg O_2/l	21.0	19.0	19.5	17.5	16.5	23.5	28.0	32.0	16.0	25.0	19.5	14.0	25.5	26.5	27.0
effluent mg O_2/l	15.5	12.0	12.5	13.5	13.5	14.5	20.5	24.0	11.5	12.5	13.0	9.0	17.5	22.5	23.0
removal %	26.2	36.8	35.9	22.9	18.2	38.3	26.8	25.0	28.1	50.0	33.3	35.7	31.4	15.1	14.8
Color															
influent mg Pt/l	40	40	60	50	60	80	80	120	60	120	100	30	100	yellow	100
effluent mg Pt/l	40	40	60	45	50	80	70	75	50	100	100	30	100	yellow	100
removal %	0.0	0.0	0.0	10.0	16.7	0.0	12.5	37.5	16.7	16.7	0.0	0.0	0.0	-	0.0
Anionic detergents															
influent mg/l	-	7.2	-	5.0	-	6.0	-	-	3.5	-	-	2.3	-	5.3	-
effluent mg/l	-	6.0	-	4.0	-	4.25	-	-	2.5	-	-	2.6	-	5.6	-
removal %	-	16.7	-	20.0	-	29.2	-	-	28.6	-	-	-	-	-	-

Table 6-7 (con.)

Date/indicator	9/24	9/25	9/26	9/27	10/01	10/02	10/04	10/05	10/08	10/09	10/10	10/11	10/15	10/16	10/17
Suspended solids															
influent mg/l	34.9	59.2	46.4	67.6	25.2	14.4	11.6	14.0	29.6	24.0	21.6	42.0	8.8	14.8	17.6
effluent mg/l	10.4	10.8	9.8	20.6	5.0	7.4	6.0	6.2	5.6	2.8	10.4	6.8	2.6	2.4	4.8
removal %	73.6	81.8	78.9	69.5	80.2	48.6	48.3	55.7	81.2	88.3	51.9	83.8	70.5	83.8	72.7
BOD$_5$															
influent mg O$_2$/l	28.0	18.6	18.3	16.7	20.0	18.9	12.0	14.6	23.3	18.6	17.8	8.3	14.3	10.2	14.5
effluent mg O$_2$/l	13.5	9.5	5.7	6.7	10.0	6.2	7.2	8.0	8.0	4.4	4.4	6.0	7.5	5.5	5.6
removal %	51.8	48.9	68.9	59.9	50.0	67.2	40.0	45.2	65.7	76.3	75.3	27.7	49.0	46.1	54.5
COD															
influent mg O$_2$/l	140.0	272.0	201.9	127.6	78.1	58.5	62.7	108.4	63.6	86.2	74.5	67.9	49.5	63.5	61.3
effluent mg O$_2$/l	88.0	96.0	18.8	93.3	47.6	41.7	50.9	92.0	49.9	58.8	49.9	50.9	40.8	46.6	50.7
removal %	37.1	64.7	41.2	26.9	39.0	28.8	18.8	15.1	21.4	31.8	32.9	25.0	17.2	27.4	17.2
Permanganate COD															
influent mg O$_2$/l	25.5	43.0	34.0	31.5	15.5	16.5	12.5	16.5	13.5	16.0	18.0	17.5	11.0	14.0	13.0
effluent mg O$_2$/l	20.0	40.0	29.0	26.0	10.5	12.5	11.0	15.0	10.0	12.5	15.0	16.0	9.5	13.0	10.0
removal %	21.6	7.0	14.7	17.5	32.3	24.2	12.0	9.1	25.9	21.9	16.7	8.6	13.6	7.1	23.1
Color															
influent mg Pt/l	60	yellow	navy blue	100	30	30	60	50	40	40	60	pink	30	60	60
effluent mg Pt/l	60	yellow	navy blue	100	30	30	60	50	30	40	60	pink	35.0	70	60
removal %	0.0	-	-	0.0	0.0	0.0	0.0	0.0	25.0	0.0	0.0	-	0.0	0.0	0.0
Anionic detergents															
influent mg/l	-	-	-	-	-	-	-	-	-	-	-	-	1.65	-	3.6
effluent mg/l	-	-	-	-	-	-	-	-	-	-	-	-	1.60	-	3.37
removal %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	6.4

Table 6-7 (con.)

Date/indicator	10/18	10/19	10/22	10/23	10/24	10/25	10/26	10/29	10/30	10/31	11/05	11/05	11/07	11/08	12/01
Suspended solids															
influent mg/l	20.4	20.0	20.4	44.6	9.2	17.4	13.6	5.6	42.8	8.4	10.08	12.0	25.02	6.4	11.2
effluent mg/l	6.4	12.0	4.0	15.6	5.4	8.0	8.6	1.8	6.6	3.2	9.2	2.4	11.8	5.0	2.6
removal %	68.6	40.0	78.4	65.0	41.3	54.0	36.8	67.9	84.6	61.9	14.8	80.0	53.2	21.9	76.8
BOD_5															
influent mg O_2/l	8.5	18.5	18.5	22.2	14.0	10.2	9.7	8.7	20.0	7.2	10.0	8.6	12.0	10.0	11.6
effluent mg O_2/l	6.0	6.8	4.4	6.1	6.2	5.3	3.7	3.2	3.2	3.8	7.6	4.3	6.7	6.1	6.6
removal %	29.4	63.2	76.2	72.5	55.7	40.8	61.9	63.2	84.0	47.2	24.0	50.0	44.2	39.0	43.1
COD															
influent mg O_2/l	53.2	47.9	46.5	105.6	26.3	50.9	57.3	44.8	97.8	56.1	74.6	61.2	75.5	-	22.9
effluent mg O_2/l	42.6	42.0	19.9	47.0	42.6	45.4	41.7	26.4	43.3	42.9	65.8	57.6	57.8	-	21.1
removal %	19.6	12.5	57.0	55.5	-	11.8	27.2	41.1	55.6	23.0	11.7	5.6	23.4	-	23.3
Permanganate COD															
influent mg O_2/l	15.0	16.5	11.0	20.0	10.0	17.0	13.5	10.5	22.5	12.0	14.0	15.0	16.0	10.5	18.0
effluent mg O_2/l	13.0	14.0	7.5	10.0	9.5	10.5	11.0	6.5	11.0	11.0	12.5	9.0	12.5	10.5	14.5
removal %	13.3	15.2	31.8	50.0	5.0	38.2	18.5	38.1	51.1	15.4	10.7	40.0	21.9	-	19.5
Color															
influent mg Pt/l	60	50	30	60	pink	50	40	30	-	-	-	-	-	-	-
effluent mg Pt/l	60	50	25	40	pink	40	40	25	-	-	-	-	-	-	-
removal %	0.0	0.0	16.7	33.3	-	20.0	0.0	16.7	-	-	-	-	-	-	-
Anionic detergents															
influent mg/l	-	-	2.5	-	4.0	-	-	2.0	-	2.7	-	-	2.25	-	-
effluent mg/l	-	-	1.9	-	2.9	-	-	1.4	-	2.0	-	-	2.2	-	-
removal %	-	-	24.0	-	27.5	-	-	30.0	-	25.9	-	-	-	-	-

Table 6-7 (con.)

Date/indicator	12/07	12/10	12/11	12/14	12/17	12/18	12/19	12/20	12/21	12/24	75 r 1/08	1/09	1/09	1/10	1/11
Suspended solids															
influent mg/l	57.2	60.0	10.4	76.8	16.0	37.6	31.6	44.4	57.6	42.0	33.2	28.4	31.2	62.4	
effluent mg/l	6.8	1.8	2.6	6.4	2.8	5.0	4.8	4.6	36.4	8.4	16.8	0.6	4.8	5.8	
removal %	88.1	97.0	75.0	88.5	82.5	86.7	84.8	89.6	36.8	80.0	49.3	97.9	84.6	90.7	
BOD_5															
influent mg 02/l	7.3	-	-	23.7	12.7	11.7	11.0	17.2	8.0	17.2	22.5	16.0	12.0	18.7	
effluent mg O_2/l	4.6	-	-	8.8	6.8	4.3	4.1	4.6	4.0	7.3	5.6	6.0	5.0	6.1	
removal %	37.0	-	-	62.9	46.4	62.0	62.7	73.4	50	57.5	70.6	62.0	58.3	67.3	
COD															
influent mg O_2/l	59.4	72.4	63.7	19.4	72.0	76.8	112.4	92.2	-	74.9	105.6	102.3	82.1	80.8	
effluent mg O_2/l	52.8	51.1	80.0	56.6	40.8	62.4	81.9	76.2	-	60.3	49.5	57.8	35.7	56.6	
removal %	11.1	29.4	-	5.3	43.2	18.8	27.1	16.7	-	19.5	5.3	43.5	56.5	30.0	
Permanganate COD															
influent mg O_2/l	12.5	15.0	13.0	28.0	12.5	20.0	21.5	20.0	13.5	12.5	16.0	19.0	13.5	17.0	
effluent mg O_2/l	11.5	12.5	10.5	15.5	9.5	14.5	16.0	14.0	11.5	9.5	10.5	12.0	11.5	10.5	
removal %	7.9	16.6	19.2	44.6	23.9	27.5	25.5	30.0	14.7	23.9	34.3	36.8	14.8	38.2	
Color															
influent mg Pt/l	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
effluent mg Pt/l	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
removal %	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Anionic detergents															
influent mg/l	-	3.8	-	2.5	2.0	-	2.0	-	-	2.2	1.75	-	1.5	-	
effluent mg/l	-	3.2	-	2.2	1.9	-	1.7	-	-	2.0	1.40	-	1.2	-	
removal %	-	15.2	-	13.6	5.0	-	15.0	-	-	9.1	20.0	-	20.0	-	

Table 6-7 (con.)

Date/indicator	1/17	1/18	1/21	1/22	1/23	1/24	3/03	3/04	3/05	3/10	3/11	3/12	3/17	3/18
Suspended solids														
influent mg/l	34.0	31.6	14.4	22.8	28.8	10.8	32.0	32.0	32.0	31.0	15.6	9.2	19.6	22.0
effluent mg/l	6.0	8.2	1.6	7.4	6.4	0.6	31.6	31.6	31.6	28.4	4.0	2.4	44.4	5.0
removal %	82.3	74.0	88.0	67.5	77.7	94.4	1.3	1.3	1.3	8.4	74.4	74.3	77.6	77.3
BOD_5														
influent mg O_2/l	17.5	23.7	27.2	11.5	-	-	18.7	18.7	18.7	11.7	11.5	9.5	21.2	16.5
effluent mg O_2/l	5.3	9.0	6.6	6.0	-	-	6.0	6.0	6.0	7.3	5.3	4.1	11.8	6.5
removal %	69.7	62.0	75.7	47.8	-	-	67.9	67.9	67.9	37.6	54.0	58.0	44.3	62.6
COD														
influent mg O_2/l	118.2	104.2	94.0	98.0	164.0	84.0	61.2	61.2	61.2	76.3	77.2	80.0	70.0	56.0
effluent mg O_2/l	74.5	78.7	72.0	69.0	74.0	40.0	36.7	36.7	36.7	59.4	63.4	57.0	38.0	42.0
removal %	37.3	16.4	23.4	29.6	5.5	5.2	40.0	40.0	40.0	22.1	18.0	28.8	45.7	25.0
Permanganate COD														
influent mg O_2/l	21.0	24.5	19.0	18.5	40.5	37.0	20.0	20.0	20.0	19.5	18.5	15.0	14.0	15.5
effluent mg O_2/l	15.5	20.0	16.0	15.0	18.5	15.0	16.0	16.0	16.0	15.5	15.0	13.0	10.0	10.5
removal %	26.1	18.3	15.7	18.9	54.3	59.4	20.0	20.0	20.0	20.5	22.0	12.9	28.6	32.3
Color														
influent mg Pt/l	-	-	-	-	-	-	60	60	60	60	60	60	80	green
effluent mg Pt/l	-	-	-	-	-	-	50	50	50	60	50	60	80	green
removal %	-	-	-	-	-	-	16.7	16.7	16.7	0.0	16.7	0.0	0.0	-
Anionic detergents														
influent mg/l	2.25	-	1.9	-	-	2.3	-	-	-	-	3.0	-	-	-
effluent mg/l	2.2	-	1.8	-	-	2.1	-	-	-	-	2.8	-	-	-
removal %	2.2	-	5.3	-	-	8.7	-	-	-	-	60.0	-	-	-

Table 6-7 (con.)

Date/indicator	3/19	3/20	3/24	3/25	4/10	4/14	4/15	4/16	4/17	4/18	4/22	4/23	4/24	4/28
Suspended solids														
influent mg/l	6.0	19.6	32.0	23.6	35.6	45.6	25.2	24.0	2.4	16.4	83.2	21.2	20.4	6.8
effluent mg/l	1.8	5.2	6.6	1.6	3.2	1.2	4.8	2.0	8.8	9.0	5.4	4.0	18.4	0.4
removal %	70.0	73.5	79.4	93.2	91.0	97.4	80.9	91.7	-	45.1	93.5	81.1	9.8	94.1
BOD_5														
influent mg O_2/l	12.0	13.5	21.7	15.5	17.5	22.5	16.0	13.5	12.3	18.0	20.5	23.0	18.0	16.5
effluent mg O_2/l	6.0	9.3	9.7	7.4	5.0	4.1	5.9	4.1	5.9	4.3	5.6	6.0	5.8	3.2
removal %	50.0	31.2	65.0	52.3	71.4	81.8	63.1	69.6	52.0	76.1	72.7	73.9	67.8	80.6
COD														
influent mg O_2/l	57.4	61.7	71.1	55.8	86.0	59.5	75.0	67.2	69.1	67.0	156.0	121.4	-	36.9
effluent mg O_2/l	41.1	46.3	41.2	35.9	48.0	23.0	46.1	41.3	42.1	36.6	80.0	75.4	-	12.0
removal %	28.3	25.0	42.1	35.7	44.2	61.3	38.5	38.4	40.0	45.3	48.8	37.0	-	67.4
Permanganate COD														
influent mg O_2/l	15.0	17.0	20.0	17.0	21.0	18.0	19.5	19.5	17.5	21.0	30.5	26.0	25.5	12.5
effluent mg O_2/l	11.0	11.0	10.0	10.0	12.5	6.5	14.0	14.5	15.0	11.0	23.0	19.5	11.0	9.5
removal %	26.7	35.2	50.0	41.2	40.5	63.9	28.2	25.5	14.3	47.6	24.6	25.0	56.9	24.0
Color														
influent mg Pt/l	60	60	navy blue	navy blue	80	40	60	blue	blue	50	green	60	60	60
effluent mg Pt/l	60	50	60	navy blue	60	30	60	blue	blue	50	green	60	50	40
removal %	0.0	16.7	-	-	25.0	25.0	0.0	-	-	0.0	-	0.0	16.7	33.3
Anionic detergents														
influent mg/l	2.62	-	-	3.2	-	2.0	-	-	3.4	-	-	-	4.0	-
effluent mg/l	2.3	-	-	2.4	-	1.8	-	-	2.3	-	-	-	2.8	-
removal %	12.2	-	-	37.5	-	10.0	-	-	32.4	-	-	-	30.0	-

Table 6-7 (con.)

Date/indicator	4/29	5/02	5/05	5/06	5/07	6/18	6/18	6/19	6/23	6/24	6/25	6/26	6/30	Average from series III	Average from series I, II, III
Suspended solids															
influent mg/l	29.2	9.2	58.0	21.0	10.8	18.0	46.8	14.4	47.2	22.0	70.6	24.8	15.2	29.7	29.6
effluent mg/l	6.8	4.5	5.2	2.0	2.6	2.8	15.4	0.6	2.2	3.2	2.6	20.2	2.2	7.8	9.7
removal %	76.7	51.1	90.3	90.5	68.5	84.4	67.1	84.1	95.3	85.3	96.3	-	85.5	69.2	60.4
BOD_5															
influent mg O_2/l	19.0	21.7	16.7	11.5	12.0	24.5	12.2	18.2	12.0	21.0	10.7	14.0	13.0	16.6	15.6
effluent mg O_2/l	2.4	1.8	3.6	2.6	2.6	5.4	3.6	2.6	4.4	4.4	3.2	3.6	5.4	6.1	6.4
removal %	87.9	91.7	78.4	77.4	78.3	78.0	70.5	85.7	63.3	79.0	70.1	74.3	58.5	61.9	55.1
COD															
influent mg O_2/l	43.2	80.6	67.3	103.7	58.5	103.4	56.0	52.5	60.2	45.4	37.1	106.2	54.2	83.9	87.4
effluent mg O_2/l	28.4	21.8	45.2	52.8	43.4	79.9	49.7	41.4	25.5	34.6	41.8	43.7	32.4	53.8	56.4
removal %	34.7	72.9	32.8	49.0	26.0	22.7	11.3	21.1	57.7	23.8	-	58.9	40.2	33.3	32.6
Permanganate COD															
influent mg O_2/l	17.5	22.0	15.0	18.5	11.5	Investigations not performed								19.0	19.8
effluent mg O_2/l	12.5	12.5	7.5	16.5	10.5									13.8	14.0
removal %	29.6	43.2	50.0	10.8	8.7									26.8	29.6
Color															
influent mg Pt/l	60	50	50	100	60	80	60	60	40	60	50	60	40	58.0	57.8
effluent mg Pt/l	50	40	40	100	60	60	60	50	30	60	40	40	20	55.0	52.9
removal %	16.7	20.0	20.0	0.0	0.0	25.0	0.0	16.7	25.0	0.0	20.0	33.3	50.0	21.0	15.9
Anionic detergents															
influent mg/l	5.6	-	7.2	-	-	-	-	-	-	0.36	0.35	-	-	3.0	3.81
effluent mg/l	4.0	-	2.3	-	-	-	-	-	-	0.36	0.35	-	-	2.3	2.31
removal %	28.6	-	68.1	-	-	-	-	-	-	-	-	-	-	22.3	29.3

Table 6-8. Effectiveness of pilot scale filtration process based on average samples performed in series IV, stage II

Contamination indicator	Influent concen-tration, mg/l	Column A			Column B			Column C			Column D		
		Effluent concen-tration, mg/l	Removal mg/l	Removal %	Effluent concen-tration, mg/l	Removal mg/l	Removal %	Effluent concen-tration, mg/l	Removal mg/l	Removal %	Effluent concen-tration, mg/l	Removal mg/l	Removal %
BOD_5 mg O_2/l													
Cycle 1	15.5	2.8	10.7	79.3	3.6	9.9	73.3	3.4	10.1	74.8	2.2	11.3	85.7
2	10.0	2.6	7.4	74.0	3.2	6.8	68.0	3.0	7.0	70.0	2.4	7.6	76.0
3	11.0	2.5	8.7	79.1	4.0	7.0	63.6	-	-	-	3.0	8.0	72.7
4	11.0	3.2	7.8	70.9	3.8	7.2	65.5	3.6	7.4	67.5	3.6	7.4	67.3
5	15.5	4.2	11.3	72.9	3.6	11.9	76.8	5.2	10.5	66.5	4.4	11.1	71.6
6	14.5	4.4	10.1	69.7	-	-	-	3.6	10.9	75.2	-	-	-
7	22.2	-	-	-	-	-	-	6.0	16.2	73.0	-	-	-
Average	14.2	3.3	-	74.3	3.6	-	67.6	4.2	-	71.2	3.1	-	74.3
COD mg O_2/l													
Cycle 1	68.0	39.0	29.0	42.6	42.0	26.0	38.2	40.0	28.0	41.2	39.0	29.0	42.7
2	60.5	20.5	40.0	66.1	54.6	25.9	42.8	14.0	46.5	76.9	14.0	46.5	76.9
3	66.2	47.5	18.7	28.3	47.5	18.7	28.5	-	-	-	46.0	20.2	30.5
4	67.4	35.6	31.8	47.2	46.8	20.6	30.6	62.7	4.7	7.0	41.5	25.9	38.4
5	70.0	45.0	25.0	35.7	35.0	35.0	50.0	37.0	35.0	47.1	45.2	24.8	35.4
6	95.4	52.4	63.0	66.0	-	-	-	31.5	63.9	67.0	-	-	-
7	63.0	47.7	15.3	24.3	-	-	-	49.7	13.3	21.1	-	-	-
Average	70.1	38.2	-	44.4	41.2	-	42.0	39.2	-	43.4	37.1	-	44.8
Permanganate COD mg O_2/l													
Cycle 1	14.5	10.4	4.0	27.6	10.5	4.0	27.6	10.5	4.0	27.6	11.0	3.5	24.1
2	13.5	9.5	4.0	29.6	9.5	4.0	29.6	8.0	5.5	40.7	10.5	3.0	22.2
3	23.5	15.5	8.0	34.0	15.5	8.0	34.0	-	-	-	15.5	8.0	34.0
4	19.5	15.5	4.0	25.8	16.0	3.0	15.4	15.0	4.5	23.1	16.0	3.0	15.4
5	17.0	12.0	5.0	29.4	11.0	6.0	35.3	12.0	5.0	29.4	12.0	5.0	29.4
6	17.0	10.0	7.0	41.2	-	-	-	9.0	8.0	47.1	-	-	-
7	15.0	13.0	2.0	13.3	-	-	-	14.8	1.0	6.7	-	-	-
Average	17.1	12.3	-	28.7	12.5	-	28.4	11.4	-	29.1	13.0	-	25.0

Table 6-8 (con.)

Contamination indicator	Influent concen-tration, mg/l	Column A Effluent concen-tration, mg/l	Column A Removal mg/l	Column A Removal %	Column B Effluent concen-tration, mg/l	Column B Removal mg/l	Column B Removal %	Column C Effluent concen-tration, mg/l	Column C Removal mg/l	Column C Removal %	Column D Effluent concen-tration, mg/l	Column D Removal mg/l	Column D Removal %
Suspended solids mg O_2/l													
Cycle 1	16.8	11.6	5.2	31.0	24.4	-	0.0	6.4	10.4	61.9	1.4	15.4	91.7
2	72.0	5.8	66.2	91.9	8.0	64.0	88.9	7.2	64.8	90.0	11.4	60.6	84.2
3	25.6	15.0	10.6	41.4	5.8	19.8	77.3	-	-	-	5.4	20.2	78.9
4	42.4	3.4	39.0	92.0	5.2	37.2	87.7	5.0	37.4	88.2	-	15.6	100.0
5	15.6	8.8	6.8	43.6	0.0	15.6	100.0	7.2	8.4	53.9	12.2	3.4	21.8
6	38.4	3.4	35.0	91.2	-	-	-	7.6	30.8	80.2	-	-	-
7	30.0	-	30.0	100.0	-	-	-	-	30.0	100.0	-	-	-
Average	34.4	6.9	-	70.2	8.7	-	70.8	5.6	-	79.0	6.1	-	73.3
Alkalinity mg/l													
Cycle 1	7.6	7.2	-	-	7.2	-	-	7.6	-	-	7.6	-	-
2	8.8	8.8	-	-	7.6	-	-	7.8	-	-	8.8	-	-
3	10.4	10.6	-	-	10.0	-	-	-	-	-	10.0	-	-
4	10.0	10.0	-	-	10.0	-	-	10.0	-	-	10.0	-	-
5	7.4	7.6	-	-	7.4	-	-	7.4	-	-	7.4	-	-
6	4.8	4.0	-	-	-	-	-	4.0	-	-	-	-	-
7	9.2	8.8	-	-	-	-	-	8.8	-	-	-	-	-
Color mg Pt/l													
Cycle 1	40	30	10	25.0	30	10	25.0	30	10	25.0	30	10	25.0
2	50	40	10	20.0	30	20	40.0	30	20	40.0	30	20	40.0
3	50	40	10	20.0	40	10	20.0	-	-	-	40	10	20.0
4	60	50	10	16.7	40	20	33.3	40	20	33.3	40	20	33.3
5	50	35	15	30.0	35	15	30.0	35	15	30.0	35	15	30.0
6	40	30	10	25.0	-	-	-	30	10	25.0	-	-	-
7	50	30	20	40.0	-	-	-	30	20	40.0	-	-	-
Average	49	19.5	-	36	35	-	30	32	-	32	35	-	30
Color threshold													
Cycle 1	25:100	35:100	-	-	35:100	-	-	35:100	-	-	35:100	-	-
2	20:100	25:100	-	-	35:100	-	-	35:100	-	-	35:100	-	-
3	20:100	25:100	-	-	25:100	-	-	-	-	-	25:100	-	-
4	15:100	20:100	-	-	25:100	-	-	25:100	-	-	25:100	-	-
5	20:100	30:100	-	-	30:100	-	-	30:100	-	-	30:100	-	-
6	25:100	35:100	-	-	-	-	-	-	-	-	-	-	-
7	20:100	35:100	-	-	-	-	-	35:100	-	-	-	-	-

Table 6-8 (con.)

Contamination indicator	Influent concentration, mg/l	Column A			Column B			Column C			Column D		
		Effluent concentration, mg/l	Removal mg/l	Removal %	Effluent concentration, mg/l	Removal mg/l	Removal %	Effluent concentration, mg/l	Removal mg/l	Removal %	Effluent concentration, mg/l	Removal mg/l	Removal %
pH													
Cycle 1	8.0	7.9	-	-	8.0	-	-	8.0	-	-	8.0	-	-
2	7.9	8.0	-	-	8.0	-	-	8.0	-	-	8.0	-	-
3	7.3	7.8	-	-	7.8	-	-	-	-	-	7.8	-	-
4	7.8	7.8	-	-	7.8	-	-	8.0	-	-	7.9	-	-
5	8.0	8.0	-	-	8.0	-	-	8.0	-	-	8.0	-	-
6	7.9	7.4	-	-	-	-	-	7.6	-	-	-	-	-
7	7.8	7.8	-	-	-	-	-	7.8	-	-	-	-	-
Anionic detergents mg/l													
Cycle 2	5.4	2.6	0.8	23.5	1.9	1.5	44.1	1.65	1.75	51.5	2.0	1.4	41.2
7	3.0	2.6	0.4	13.3	-	-	-	1.8	1.2	40.0	-	-	-

Table 6-9. Results of physicochemical analysis in series V, stage II

Kind of containment indicator		Cycle 1 (11/17/75)			Cycle 2 (11/29/75)		
		Influent concentration	Effluent concentration	Removal, %	Influent concentration	Effluent concentration	Removal, %
BOD_5	mg O_2/l	20	11.2	44.0	45.7	34.0	25.6
COD	mg O_2/l	132.9	94.0	29.3	181.2	85.4	52.9
Oxygen permanganate COD	mg O_2/l	38.2	35.3	7.6	30.4	30.0	1.3
Suspended solids	mg/l	36.5	3.4	90.7	40.9	9.4	77.0
Alkalinity	mval/l	23.8	23.5	-	17.6	18.1	-
Color	mg Pt/l	pinkish	pinkish	-	40.0	50.0	-
Detergents	mg/l	0.354	0.309	12.7	0.38	0.53	-
pH		8.75	8.60	-	9.2	9.2	-
Ammonia	mg N_{NH_4}/l	-	-	-	0.38	0.38	-
Nitrates	mg N_{NO_3}/l	-	-	-	0.750	0.696	7.2
Nitrites	mg N_{NO_2}/l	-	-	-	0.122	0.091	25.4

Table 6-10. Washing conditions of operation of a dual media filtration bed in relation to the cycle of filtration. Granulation of the bed according to the curve in figure 6-7, column B, series V, pilot scale

Date of investigations	Filtration cycle parameters			Bed washing parameters					Mean suspended solid content in washings		Ratio of washing media to filtered wastewater		Water consumption in relation to filter
	Rate of filtration	Cycle duration time at max. pressure losses= 165 cm	Decrease of suspended solids content in wastewater, mg/l	Medium	Medium temperature, °C	Washing intensity, m^3/m^2h	Washing time, min	Expansion sand/anthracite, %	mg/l	Load, g	Water	Air	
11/14/75 r	5.1	28	33.1	water	8	67	5.2	25/40	245.7	201 x 245.7 = 49 g	7.85	-	11.35
				air	-	-	-		-				
				water	8	67	5.2	30/50					
11/14/75 r	15	13	31.5	air	-	105.0	1.08	10/30	502.5	140 x 502.5 = 70 g	5.35	1.38	4.52
				water	8	107.0	4.4	40/80					
12/12/75 r	5.1	22	-	air	-	104.5	1.08	10/30	603.0	130 x 603 = 78 g	6.45	1.78	3.95
				water	8	58.5	7.5	25/70					
12/13/75 r	5.1	18	-	water	8	60.0	9.25	25/70	458.5 x 458.5 = 75 g	162.5 x	10	-	10.1

SECTION 7

COAGULATION

INTRODUCTION

Description of the Problem

Wastewater treatment in the coagulation process can occur by means of: floculation and sedimentation of suspended solids contained in the wastewater; precipitating salts or complex compounds, which dissolve with difficulty as a result of the reaction with coagulant cations; or adsorption of dissolved substances on newly formed solid phases, that is, flocs of metal hydroxides.

The effectiveness of the treatment in the coagulation process depends on the kinds of pollutants in the wastewater. Biologically treated wastewater may contain a high concentration of refractory compounds. In the combined municipal and textile wastewater at Andrychow, the main source of refractory substances is the textile plant. The composition of industrial wastewater depends on the raw materials, the chemicals, and the production processes used.

On the basis of knowledge of the technological processes and chemicals used in textile production, it is possible to draw conclusions about the kinds and amounts of chemical pollutants in the wastewater. The chemical structures of these pollutants determine whether they can be removed from the wastewater during the coagulation process. The chemical substances used in production can pass to wastewater in unchanged form or in changed form resulting from their use in such production processes as hydrolysis and oxidation.

Interaction of Chemical Pollutants and the Coagulation Process

The following analyses were undertaken to determine both the possibility of removal by coagulation and the influence on the coagulation process of chemical compounds used in the ACP. These compounds are divided into organic and inorganic types.

Organic Compounds--

Dyes--The percentage amounts of dye content of different groups in their total mass is given in table 7-1. From this data it is clear that the amounts of certain groups of dyes are relatively small, and therefore, that they will not have great influence on the quality of the discharged wastewater.

Wastewater dyes (sulfur, vat, and indigosols, which are transformed into vat dyes after chemical changes) pass in alkaline and reducing media to waste water in dissolved form. Decrease of pH in the oxidizing medium causes chemical changes. As a result of these, a form of these dyes that is difficult to dissolve in water appears [30].

Dispersed dyes, which are insoluble in water, pass to wastewater from the reducing cleaning process in an alkaline medium. In a nonalkaline medium, dispersed dyes are less soluble in water. Dyes that are in an undissolved form as a result of mixing with other portions of wastewater can be subject to dissolution, thus increasing the wastewater color. The majority of dyes used in the ACP, as a result of decrease in pH in oxidizing conditions, are transformed into compounds difficult to dissolve in water. From this, it is clearly possible to change part of the dyes in wastewater into solid form by altering pH and preliminary oxidation. These changes make further removal by means of coagulation possible.

Formation of complex compounds--A number of chemical compounds used for production, including dyes, contain ligand structures formed by atoms of oxygen, nitrogen, and sulfur. These structures are capable of joining with metal cations into complex compounds. An appropriate structure of atom groupings causes the formation of neutral complexes called inner-complex salts. Compounds of this type are characterized by low solubility in water. Their formation during coagulation is encouraged by a decrease in wastewater pH, which increases the concentration of ions of complexing metal. This makes it possible to use coagulation to isolate compounds that are difficult to dissolve. Binding of the coagulant ions into complexes soluble in water can also occur, causing secondary wastewater pollution.

Sorption of dissolved dyes on precipitated hydroxide sediment--Most dyes contain acid groups which form anions on account of dissociation in water. Precipitated hydroxide flocs have an adsorptive capacity. According to the adsorptive-coprecipitative theory, the process of enrichment of the solid phase in the adsorbed substance depends on the field of electric forces formed on the surface of the solid body. An equilibrium is established between the ions forming the outer side of the double layer and the ions of the solution [31]. In positively charged colloids, anions form on the outer side. Anions of the dye can be subject to adsorption on this layer.

A condition of sorption during coagulation is the formation of positive potential on the hydroxides. In wastewater in which negative colloids appear, the charge after the adding of coagulant depends on the sum of the charges in the dispersed phase. It is clear from this that the coagulant dosage should be greater than the optimal one determined for the removal of colloids from wastewater. The decrease of the pH of the medium has a great influence on the increase of the positive charge of the metal hydroxides used for coagulation. Therefore, sorption during coagulation increases as the pH of the wastewater is decreased.

Surface-active agents--The anionic detergents used in the ACP possess average resistance to the action of hard water. Thus, their partial removal is possible: during coagulation, in the form of salts that are difficult to dissolve; and during adsorption, in the form of anions of surface-active agent on precipitated sediment.

Nonionic detergents are susceptible to sorption on suspended matter. As a result of sorption on newly formed flocs during coagulation, they can be removed from wastewater.

Organic complex-forming compounds--The technological processes use organic compounds that bind divalent and trivalent ions of metal in the form of soluble complexes. The presence of these compounds in wastewater causes a decrease of the amount of precipitated hydroxides and causes secondary pollution of wastewater with metal ions of the coagulant.

Inorganic Compounds--

The large consumption of carbonates and hydroxides in fabric finishing causes an increase in the alkalinity of the wastewater. Low CO_2 content with high alkalinity can cause calcium carbonate to be precipitated in the wastewater. The sudden decrease in the pH of the wastewater during coagulation can cause the isolation of CO_2 gas, which leads to flotation of coagulated sludge (or poor sedimentation).

From the washing processes, phosphorous and silicate ions pass to the wastewater. During coagulation these should be removed through the formation of difficult-to-dissolve salts. A decrease in the wastewater pH to about 6 leads to the precipitation of phosphorous. During coagulation the $Cr3^{+}$ ion content should be reduced through coprecipitation with discrete flocs.

In the coagulation process suspended solids can remain removed from the wastewater, as can partially dissolved compounds that are in large part susceptible to precipitation through sorption on precipitated hydroxides. Some compounds in textile wastewater can, however, hinder the coagulation process.

Coagulation as the Unit Process for Textile Wastewater Treatment

Coagulation ranks among the most efficient methods of treating colored wastewater [32]. In general, it precedes the biological treatment process and is carried out on isolated wastewater from the dyehouse or general wastewater from the whole textile plant. An effective coagulant for treating wastewater from the dyehouse is ferrous sulfate in amounts of several hundred mg/l, with calcium added. The Niers method based on the use of iron chips is also effective [33]. Good results are also obtained using aluminum sulfate, ferrous sulfate, and ferric sulfate or ferric chloride. The optimum pH ranges for individual coagulants are: for aluminum sulfate, pH about 6; for ferric sulfate, pH from 4.5 to 6; for ferrous sulfate, pH from 8.5 to 10 [34]. Aluminum and ferric salts also precipitate synthetic detergents of the alkylarylsulfonate type [34]. Chemical treatment of general textile wastewater usually achieves over 50 percent removal of color [35]. Removal of individual dye substances by coagulation is variable, from 0 to over 90 percent, averaging 50 to 70 percent for a dye mixture [36].

To obtain an 80 to 90 percent reduction of detergents, the necessary dose of $Al_2/SO_4/_3 \cdot 18\ H_2O$ (alum) for 1 mg of surface-active agent is from 16 to 25 mg [37]. The use of a mixture of salts Al^{3+}, Fe^{3+}, Fe^{2+}, and Ca^{2+} for removing detergents and color from textile wastewater gave better results than the use of one electrolyte [37]. According to the investigations into coagulation of mixed municipal and textile wastewater, the necessary dose of aluminum sulfate for coagulation of wastewater without previous biological treatment was 1,000 mg/l of alum; the dose for wastewater after biological treatment was 500 mg/l of alum with final color of 15 to 60 mg/l Pt [1, 38]. The process of coagulating strongly colored wastewater is made more difficult by dissolved iron compounds remaining in the solution. After dilution these cause secondary coagulation in the receiving stream [39].

OBJECTIVES

The large number of factors that influence the composition of textile wastewater and its susceptibility to coagulation justifies investigation into the use of the coagulation process. This research was carried out on both a laboratory and a pilot scale, from 1974 to 1976, on mixed biologically treated wastewater containing refractory pollutants from textile wastewater. A series of tests was performed, taking into account the different factors that indicate whether the coagulation process is suitable for removing pollutants from textile wastewater.

The detailed objective of investigations included a determination of:

- the kind of coagulant used,
- the influence of coagulant dosage on the removal of specific refractory pollutants from the wastewater,
- the influence of wastewater pH changes during coagulation on the results,
- the possibility of increasing the effectiveness of coagulation through preliminary oxidation,
- the influence of the level of wastewater pollution on the course and effects of the process,
- the method of carrying out the process on a larger scale, and
- the kind of technological systems suitable for the optimal course of the process.

LABORATORY INVESTIGATIONS

Test Investigations on the Choice of Coagulant

Aim and Scope of Research--

The purpose of the tests was to determine the kinds and doses of coagulants necessary for removal of suspended matter and colloids from the Andrychow wastewater. The doses that were determined, however, are insufficient for the removal of part of the dissolved substances susceptible to sorption on precipitated hydroxide flocs.

In the series of investigations carried out in June 1975, three coagulants, $FeSO_4 \cdot 7H_2O$, $FeCl_3 \cdot 6H_2O$, and alum were used. The investigations involved 12 wastewater samples characterized by the following ranges of primary pollutant indicators:

pH: 7.5 to 8.2
COD: 60 to 100 mg/l
Suspended solids: 15 to 50 mg/l
Color: 40 to 80 mg/l of Pt

Procedure--

All laboratory tests were performed by the batch method in beakers (jar tests) with a sample volume of 0.5 l. During mixing, different doses of a 5 percent solution of coagulant were added to the wastewater samples. The doses applied were 40, 80, 120, 160, and 200 mg/l in terms of the hydrated product. After chemicals were added, the wastewater was mixed slowly for 20 min and then was left for half an hour for sedimentation. Evaluating the turbidity of the wastewater samples before and after the process was made more difficult by the appearance of color and its changes as a result of coagulation. Therefore, the sample of decanted wastewater was compared visually with the standard sample obtained with coagulation and filtration. Turbidity was accepted as a criterion of the effectiveness of the process.

Discussion of Results--

For both $FeCl_3 \cdot 6H_2O$ and alum, the optimal dose for the removal of turbidity was 80 mg/l. For $FeSO_4 \cdot 7H_4O$, the required dose exceeded 200 mg/l in most cases.

The ferrous salts produced a secondary pink color. Because of this and because of the high concentration of $FeCl_3 \cdot 6H_2O$, further laboratory and pilot research into the coagulation process used alum.

Test Investigations on the Influence of Time on Removal of Color from Wastewater

Aim and Scope of Research--

Dissolved color substances are removed from wastewater by means of the precipitation of sediment and of adsorption. The time these processes require should be determined before going on to larger scale studies of the course of coagulation.

Investigations were carried out on three samples of wastewater in 1975 and were repeated in the same series in 1976, using alum.

Procedure--

Doses of coagulant were taken in amounts of 100, 200, and 300 mg of alum. Wastewater reaction was maintained at two pH levels (6.5 and 7.5) measured after coagulation, using hydrochloric acid for pH adjustment. Batch portional samples in beakers were performed as before. During mixing, a 5 percent solution of coagulant was added to the wastewater. After 3, 6, 10, 15, and 20 min, samples were collected for analysis. The color of biologically treated and coagulated wastewater samples was determined, after centrifuging the suspended solids, by measuring extinction at 400 nm. For individual doses, different pH values, and different times, the degree of color removal was calculated as the arithmetic mean for six wastewater samples. Taking the degree of color removal after 20 min as equal to 1, the relative removal values for other times were calculated. The results are plotted on a graph (figure 7-1) representing the relative increase of color removal with time.

Discussion of Results--

From the curves on figure 7-1, it is clear that removal of color from wastewater occurs in a period of about 10 min. After this time no color changes were observed.

Test Investigations on the Influence of Preliminary Oxidation Changes in Wastewater pH and of Coagulant Dose on Color Removal

Aim and Scope of Research--

The majority of dyes used in the ACP are difficult to dissolve with decreased wastewater pH and in oxidized form. Initial oxidation of the dyes accompanied by a simultaneous decrease in pH should lead to better removal in the coagulation process. Studies to confirm this hypothesis were carried out in 1975 on the six wastewater samples. As before, alum in doses of 100, 200, 400, and 600 mg/l was used.

When the test investigations on the influence of oxidation on color removal were repeated in second half of 1976, some changes in the characteristics of biologically treated wastewater took place. Iron appeared in amounts of several milligrams per litre, and the wastewater color changed to pink. In the 1975 research, it was found that the wastewater spectrum was continually diminishing and that at wavelengths above 500 nm very low extinction values (close to zero) appeared. The pink color of the wastewater in 1976 resulted in high extinction values at wavelengths above 500 nm.

Procedure--

The investigations in 1975 were carried out for three values of pH determined after the course of coagulation. The pH was controlled using hydrochloric acid. After 15 min of mixing and half an hour of sedimentation, the coagulated samples were centrifuged, and color was determined spectrophotometrically. The percentage decreases of extinction calculated in individual samples are presented in figures 7-2 and 7-3. The average values from the results for six samples are given in figure 7-12.

In the oxidation tests before reducing pH by means of HCL, NaOCl was added to the samples in doses of 8, 16, and 24 mg/l as Cl_2. The necessary contact time for a color change after the adding of oxidizer was 3 to 5 min. Next, the reaction was corrected and the coagulant added. Further procedure was the same as before. The extinction decreases in individual samples were calculated as shown on figures 7-4, 7-5, 7-6, 7-7, 7-8, and 7-9; the arithmetic means from these results are shown in figures 7-13, 7-14, and 7-15. At the same time, the influence of oxidizing only with pH correction, without coagulation, was examined. The results of this series are given in figures 7-10 and 7-11. Average results are given in figure 7-16.

The investigations in 1976 were carried out for six wastewater samples. A coagulant dose of 200 mg/l of alum was applied. The wastewater pH after coagulation was decreased to 6.6 by means of HCl. The wastewater was coagulated both without preliminary oxidation and with preliminary oxidation with NaOCl in doses of 10, 20, 30, and 40 mg of Cl_2/l. Extinction was determined at two wavelengths: 400 nm and 500 nm. The results obtained for 400 and 500 nm are presented in figures 7-25 and 7-26, which plot the removal of colored substances against the dose of oxidizer applied.

Discussion of Results--

At wastewater pH values of more than 6.5, the considerable influence of dose size on color removal is evident, particularly for doses up to 400 mg/l. The influence of dose is small at pH values around 5.8.

A decrease in wastewater pH from 7.5 to 6.5 causes an increase in color removal in the whole range of doses. For a pH of 6.5, the average increase is 20 percent. Further decrease in pH to about 5.8 causes an increase in color removal: with a dose of 100 mg/l of alum, removal averages 30 percent; with a dose of 600 mg/l of alum, removal averages about 15 percent. It should be noted that pH changes in biologically treated wastewater without coagulation did not cause significant color changes.

The effect of the action of oxidizer alone depends on pH. This is confirmed by the averaged values (figures 7-12 and 7-13). Reduction in pH with the same doses causes a small increase in color removal. An increase in the dose of oxidizer causes small changes in color removal.

In summing up, it can be asserted that the coagulation process preceded by oxidation increases the effectiveness of color removal without preliminary oxidation and with oxidation alone, especially for lower wastewater pH values. Increasing the oxidizer dose to above 16 mg of Cl_2/l does not appreciably increase color removal, especially with coagulant doses higher than 200 mg of alum.

In table 7-2 are given the color removal results for a dose of oxidizer of 8 mg of Cl_2/l both without coagulant and with a coagulant dose of 200 mg/l with and without oxident, as a function of wastewater pH.

The oxidation of wastewater before coagulation allowed for a reduction of coagulant dose at the same time it achieved a high percentage of color removal.

The results obtained in 1976 show that coagulation without previous oxidation more effectively removes substances that cause color at low wavelengths (400 nm). The average removal was about 50 percent. Preliminary oxidation is effective in removal of color which gives extinction at higher wavelengths (550 nm).

Test Investigations on the Effect of Coagulant Dose and Wastewater pH on the Removal of COD

Scope of Research--

In order to determine the influence of coagulant dose and wastewater pH on the removal of organic substances determined by COD, four series of tests were performed in 1975 and three series in 1976. Doses of 100, 200, 300, and 400 mg/l of alum were used. Wastewater reaction after coagulation was about 7.4, 6.5 and 5.8. The research method was the same as in the previous tests. The results obtained are presented on graphs on which percentage removal of COD is plotted against coagulant dose for individual wastewater pH values after coagulation (figures 7-17, 7-18, 7-19, and 7-20); the average values of this function are given on figure 7-21.

Discussion of the Results--

An increase of coagulant dose with a pH of 7.4 and 6.5 causes a parallel increase of COD removal that is particularly clear in the range of doses from 100 to 300 mg/l. With a pH of 5.8, dose increase causes an increase of COD removal; such removal, however, is less than at higher pH values. A decrease of wastewater pH from 7.4 to 6.5 causes an increase of COD removal of about 20 percent. A further decrease to a pH of 5.8 increases COD removal with a pH of 6.5 by about 10 percent.

Test Investigations on the Effect of Preliminary Oxidation of Wastewater on Removal of COD Loads

Scope of Research--

Studies were carried out for six wastewater samples. A dose of 200 mg/l of alum was used. Wastewater pH after coagulation was about 6.6. The wastewater was initially oxidized by means of doses of NaOCL: 5, 10, 20, and 30 mg of Cl_2/l. The research method was the same as before. The results are given on figure 7-19, which indicates dependence of percentage COD removal on size of oxidizer dose.

Discussion of Results--

The initial COD of the wastewater fluctuated from 60 to 92 mg of O_2/l. In most samples a decrease in percentage reduction was found with oxidizer doses up to 10 mg of Cl_2/l. Larger doses of oxidizer caused an increase in COD removal from the wastewater. However, it should be stated that in these samples the oxidizer was not removed before carrying out the chemical analysis. Increase of COD removal as an effect of the influence of residual oxidizer on COD determination did not exceed 5 mg of O_2/l when the maximum dose of NaOCl was applied.

Test Investigations on the Effect of Coagulant Dose and Wastewater pH on the Removal of Nonionic Detergents

Scope of Research--

In biologically treated wastewater, a large nonionic detergent content (about 10 mg/l) was found. The possibility of removing nonionic detergents by means of coagulation was studied, and the influence of pH change and coagulant dose on this process was determined. The research was carried out in 1975 with five samples of biologically treated wastewater.

Procedure--

The wastewater pH was decreased to 7.5, 6.5, and 5.8, using hydrochloric acid. Doses of 100, 200, 300, and 400 mg/l of alum were used. The coagulation process was performed as in previous tests.

The results of removal of nonionic detergents according to the coagulant dose used with different pH values are given in figures 7-20 and 7-21, and the mean arithmetic values in figure 7-22.

Discussion of Results--

Increasing coagulant doses at wastewater pH of 7.4 and 6.5 causes an increase of detergent removal. At a wastewater pH of about 5.8, the amount of nonionic detergents removed above a dose of 100 mg/l does not depend on the amount of coagulant. Decrease in wastewater pH during coagulation causes a considerable increase in removal of nonionic detergents. For example, the results obtained with a dose of 100 mg/l for three wastewater pH values are: for a pH of 7.4, 42 percent removal; for a pH of 6.5, 62 percent removal; for a pH of 5.8, 80 percent removal.

Test Investigations on the Influence of Preliminary Oxidation by Means of NaOCl on the Removal of Nonionic Detergents

Scope of Research--

In earlier test investigations it was found that introductory oxidation has a positive influence on removal of color during coagulation.

The present studies were carried out in 1976 for six samples of biologically treated wastewater, using a coagulant dose of 200 mg/l and one wastewater pH amounting to about 6.6. Coagulation tests were carried out with preliminary oxidation in doses of 5, 10, 20, and 30 mg of Cl_2/l of NaOCl. The procedure was the same as in previous test investigations. The results are given in figure 7-23.

Discussion of Results--

The effectiveness of removing nonionic detergents by means of coagulation without introductory oxidation depends on the initial concentration of detergents in the wastewater. Introductory oxidation with doses of about 5 mg of Cl_2/l increases removal considerably. Increasing oxidizer doses above 5 mg/l causes a reduction of detergent removal. A particularly unfavorable effect of increased oxidizer dose appears at lower concentrations of detergents in the samples.

Occurrence of Residual Aluminum Ions in the Form of Soluble Compounds and Possibility of Their Removal by Oxidation

Scope of Research--

These studies were carried out in connection with the supposition that in biologically treated wastewater there can be organic compounds capable of binding aluminum ions in the form of soluble complexes in wastewater. The studies, carried out several times during 1976 on 14 wastewater samples, depended on coagulation of wastewater with different doses of alum at different pH values in the final process. The coagulated wastewater was filtered, and the content of residual aluminum in the solution was determined. Next, the possibility of precipitating aluminum in a hydroxide form by oxidation was studied.

Procedure--

The tests on removal of residual aluminum were carried out using one coagulant dose of 200 mg/l and wastewater with a pH of 6.6. Oxidizer doses of 10, 20, 30, and 40 mg of Cl_2/l were applied. In the first series of investigations the influence of preliminary oxidation on the residual aluminum content was determined. Accordingly, after the addition of oxidizer the wastewater was coagulated, and after sedimentation and filtration the aluminum was determined. In the second series of investigations the above-mentioned doses of NaOCl were added after coagulation, sedimentation, and filtration of the wastewater. After a half-hour contact time, the samples were filtered and the residual aluminum in the filtrate was determined.

Discussion of Results--

Aluminum content in wastewater after the coagulation process is large and can cause secondary pollution of the wastewater. The results presented in table 7-3 refer to a sample for which the COD was above 140 mg/l of O_2.

Removal of aluminum by oxidation in samples in which coagulation was preceded by oxidation showed no decrease of aluminum content after the process. In many samples, after the coagulation process the aluminum concentration was higher than in samples in which coagulation alone occurred.

The results of the second series of investigations--coagulation followed by oxidation--are presented in figure 7-24. It is clear from these that the necessary dose of NaOCl for precipitation of the aluminum from the compounds is about 20 to 30 mg of Cl_2/l. The final concentrations of dissolved aluminum in the wastewater after the process are lower than 1 mg/l.

Test Investigations on the Possibility of Flotation of Post-Coagulation Sludge

Aim and Scope of Research--

During laboratory investigations, in some cases coagulated sludge floated on the wastewater surface. Studies were carried out to determine the factors that influenced this phenomenon.

The wastewater was poured into four beakers. Next, a dose of hydrochloric acid was applied to reduce the wastewater pH within the limits of 5.8 to 7.5. A 200-mg dose of alum was added as coagulant. The wastewater sample was mixed for 15 min; after a 20 min interval, sludge was observed in the samples. The quantity of floating sludge was determined both by eye and by weight several times.

Discussion of Results--

Only solid bodies whose external surfaces have a nonionic character have the natural capacity to float. Natural flotation of a solid body can occur if its surface is covered by hydrocarbons or similar groups, plus an active group which makes it possible to fix the hydrocarbon or similar substance on the surface of the solid body. During coagulation, adsorption of acid pollutants occurs on the surfaces of original suspended solids and isolated hydroxides. As a result of these processes, coagulated particles float naturally. During the investigations it was found that flotation does not take place when the pH is above 6.8. Decreasing the pH value to below 6.8 caused an increase in the amount of floating sludge; presumably, an increase in pollutant adsorption also occurred with the reduction of wastewater pH. A factor conditioning the appearance of flotation is the formation in the suspended solid of gas bubbles, which, by clinging to the surface, cause the solid body to be carried away. During coagulation acid reacts with carbonates or base carbonates to release gaseous CO_2. The amount and rate of CO_2 release is dependent on the amount of acid that binds with the final wastewater pH. Therefore, decreasing the pH increases the rate of CO_2 release, which in turn intensifies flotation. In wastewaters with high alkalinity, with which the appearance of carbonates in a solid form is connected, the quantity of sludge flotation is increased by pH reduction.

SUMMARY OF RESULT OF LABORATORY TEST INVESTIGATIONS

The test investigations were carried out at different times with varying loads of activated sludge and varying composition of wastewater flowing to the biological treatment plant. The investigations confirmed the influence of different factors on removal of refractory substances originating from textile wastewater. The following conclusions can be drawn from the test investigations:

1. Before treatment of textile wastewater by coagulation with alum, preliminary processes should be applied to decompose substances capable of forming soluble complexes with aluminum ions. When complexes are formed, it is possible to precipitate aluminum by oxidation after the coagulation process.
2. The dose of coagulant should be greater than that used for the removal of suspended solids from wastewater. The removal of color, nonionic detergents, and COD increases as the dose of coagulant is raised to a certain limit. Beyond this limit, changes do not cause, in practice, any increase of treatment efficiency.
3. Decrease in wastewater pH during coagulation in the tested pH range (5.8 to 7.5) has a positive influence on the removal of color, nonionic detergents, and COD.
4. Preliminary oxidation of wastewater increases the effects of color removal from wastewater. Low oxidizer doses (up to 5 mg of Cl_2/l) also cause up to a 20 percent increase of removal of nonionic detergents. Larger doses do not cause changes in relation to coagulant without oxidation. However, preliminary oxidation with low doses of oxidizer reduces COD removal from the wastewater by about 10 percent.

RESEARCH AT THE ANDRYCHOW EXPERIMENTAL PILOT STATION

Scope of Research

Parallel with batch test investigations on the laboratory scale, continuous investigations were carried out at the experimental pilot station in Andrychow. The aim of these was to determine the method and parameters for continuous coagulation in a full-scale installation. Biologically treated wastewater was coagulated by means of alum by two methods:

1. Contact coagulation, depending on the addition of coagulant salt to the wastewater influent to the upflow multi-layer sand filter;
2. Conventional coagulation in a reactor with suspended flocs. This depends on the flow of wastewater with added coagulant through the suspended flocs layer in which the flocculation and sedimentation occurred. After this process the wastewater was filtered on an anthracite-sand bed.

Supplementary test investigations were also carried out on the hydraulics of flow through the filtration columns used for contact coagulation.

During investigations on contact coagulation, the following conditions of operation were determined: granulation and height of the filtration media, coagulant dose, filtration rate, and backwash rate, which was adjusted to maintain 50 percent of expansion. For coagulation in the reactor with suspended flocs the following parameters were determined: coagulant dose, and wastewater flow rate through the layer of suspended flocs. With reference to laboratory investigations, the influence of decreased wastewater pH and preliminary oxidation on the treatment effects was studied.

Research Method

The investigations at the pilot station were carried out in 1975-1976, in series, in a continuous manner, generally for 6 days a week. The duration of one series of investigations was dependent on the results obtained, which were analyzed concurrently with the operation of the system, and on the range of changes in biologically treated wastewater content.

Description of Model Apparatus

Biologically treated wastewater flowed through the de-aerating tank, from which it was collected by pumps with regulated efficiency. Chemicals in the form of solutions were added to the suction pipe before collection by the pumps. Chemicals and wastewater were mixed in the pump and in the pipes feeding the wastewater to the model installation. The time the wastewater was kept together with the chemicals before being fed to the installation was varied by changing the length and diameters of the feeding conduits. In investigations that took into account introductory oxidation by the addition of NaOCl, wastewater flowed through the mixing tank. The wastewater was kept in the tank for 15 min. In research during 1976, NaOCl was fed to the suction pipe with other chemicals.

The columns for contact coagulation were constructed from a pipe of transparent Plexiglas 150 mm in diameter (figure 7-27). The wastewater was fed upward through the perforated bottom supporting the filtration media. Water for backwash flowed according to the direction of wastewater flow. A drain for the washings was fitted at the highest point of the column. The reactor with suspended flocs is presented in figure 7-28. The wastewater together with chemicals flowed from the bottom of the reactor through the 1.5-m layer of suspended flocs. The surplus sludge flowed to a side tank equipped with a sludge level indicator. The sludge was periodically discharged from this tank. The settled wastewater flowed off in the upper part through the overflow to the tank, from which it flowed downward by gravity to the filtration column. The filtration column was constructed of a transparent pipe 150 mm in diameter.

Chemical Used--
For coagulation of wastewater at the experimental plant, dissolved aluminum sulfate was used initially in a concentrated solution of 4 to 8 percent, depending on the amount of coagulant added, resulting in a concentration of 180 to 300 mg/l in the final solution.

The aluminum concentration in the solutions dosed was periodically checked. Hydrochloric acid of 2 to 6 percent concentration, depending on the alkalinity of the wastewater, was used to decrease the wastewater pH. A 5 percent solution of NaOCl was used for wastewater oxidation.

Analytical Method--
Physicochemical analyses of the biologically treated and coagulated wastewater samples were performed from daily average samples taken once every hour. The analysis covered the following pollution indicators: pH, total alkalinity, permanganate COD, dichromate COD, suspended solids, color in mg of Pt/l, and color threshold. In 1975 and 1976, anionic detergents were determined at random by the method using methylene blue, and in 1976 nonionic detergents were determined according to the method described in Section 4. In 1975 color was determined spectrophotometrically by the generally accepted method through determination of the average extinction. During 1976, after the appearance of red color, extinction was only determined at two wavelengths: 400 nm and 500 nm.

Method of Interpreting Results

In interpreting results, it was assumed that the distribution of variability of wastewater parameters before and after treatment is close to the normal Gauss distribution. In general, a straight line was obtained on diagrams of accumulated probability, showing that the distribution of results was in accordance with the normal distribution. The intersection of the straight line with the horizontal line corresponding to 50 percent of cumulative value gave a mean value from the data. From the difference between the value corresponding to 84.13 percent frequency and the average value, the standard deviation was estimated.

Test Investigations of Wastewater Flow Time Through Filtration Columns Used for Contact Coagulation

The filtration column in the coagulation process with simultaneous upward filtration can be treated as a reactor in which floc precipitation reactions occur.

The time the liquid is in the column influences the degree of sediment precipitation in the free spaces of the bed. The average time of wastewater retention in the column is calculated from the formula:

$$T = \frac{V}{q} \quad , \tag{1}$$

where: V = volume of free pores in the bed,
T = time, and
q = amount of wastewater flowing in a unit of time.

In fact, the periods of time in which particles of liquid are retained in the bed differ according to the filter media and hydrodynamic conditions, as well as the molecular and vertical diffusion and influence of viscosity. When the liquid is flowing in the columns through the granular bed, the velocity along the radius of the column increases on account of the wall effect. Deviations from the flat profile of velocity grow as the dp/dr ratio is increased, where dp is the diameter of the grains of the media, and dr is the diameter of the pipe. The wall effects grow more intense as the porosity of the system increases.

During coagulation with simultaneous filtration from the bottom, the wall effects in the model apparatus can have a great influence on the results because the ratio of the diameters of the media particles to the diameters of the columns can be large.

Research Method--

The investigations were carried out on a 150-mm diameter column. The following layers formed the column granulation:

depth of 0.15 m--gravel with 2 to 4 mm granulation
depth of 1.50 m--sand with 1.2 to 2 mm granulation
depth of 0.15 m--sand with 0.4 to 0.8 mm granulation.

At 0.05 m from the upper surface of the bed, a perforated partition was installed through the whole section of the column. A mixer was placed under the partition to equalize the concentrations of indicators flowing from the bed. The liquid was collected continuously from the space between the bed and the perforated partition by means of a pump. A dye, soluble in water and having no sorptive capacities on sand, was added to a container of clean water. The colored solution was forced into the column with varying intensity in individual series, and variable filtration speeds were obtained.

While the colored solution was being introduced, samples were collected continuously from below the perforated bottom of the column. The appearance of dye in the lower part of the column was used as the beginning of measurement of flow time through the column. At the same time, samples were collected continuously in test tubes from below the upper partition of the column, and the times of their collection were noted.

After one flow intensity in a series was completed, the column was thoroughly rinsed with water to remove indicators. The experiment was repeated with a different flow intensity.

Discussion of Results--

For the stated average bed porosity equal to 0.38, the volume of the free spaces was 12:1.

For individual filtration rates, the time the liquid was in the column was calculated, assuming that there is a uniform flow:

$q_1 = 6.0\ \mathrm{m^3/m^2h}$, $T_1 = 7$ min

$q_2 = 4.6\ \mathrm{m^3/m^2h}$, $T_2 = 9$ min

$q_3 = 3.0\ \mathrm{m^3/m^2h}$, $T_3 = 13.5$ min

$q_4 = 2.0\ \mathrm{m^3/m^2h}$, $T_3 = 21$ min .

The results for individual flow rates were plotted on a graph showing the relation of the concentration of the indicator in the column outflow in percentage and the ratio $\frac{T_s}{T}$, where T_s is the time of collecting samples and T is the average time determined from equation (1). The curves are presented in figure 7-29. On the basis of the results, it can be stated that the flow in the column under investigation diverges considerably from the conditions of pressure flow. For a filtration rate of 6 m^3/m^{2}h, about 70 percent of the liquid stays in the column less than the average time. For a speed of 4.6 m^3/m^{2}h, about 64 percent of the liquid stays in the column less than the average time, and 10 percent passes through the bed in 7.2 min. Large differences were not found between the flow rates of 2 and 3 m^3/m^{2}h. On average, 50 percent of the liquid passed through the column in a time less than the average. Curves of the concentration of indicators for these flow rates can close to the theoretical value (1). This shows that the flow through the bed was coming closer to the conditions of plug flow. It follows that the filtration rate through the experimental system under investigation should not exceed 3 m^3/m^{2}h, so that the real flow time achieved makes possible the precipitation of coagulant sludge in the whole wastewater volume in the column.

Course of Pilot Investigations and Discussion of Results

Systems of Contact Coagulation--

Technological investigations of contact coagulation were carried out for a number of systems which differed in construction and filter media size.

In system A the individual layers of the filtration media had the following composition and size:

layer 0.25 m high--gravel d = 6 to 8 mm
layer 0.45 m high--gravel d = 3 to 5 mm
layer 0.65 m high--sand d = 1.2 to 2 mm
layer 0.20 m high--sand d = 0.4 to 0.8 mm

The process was conducted in two identical columns. The coagulant dose was 150 to 180 mg of alum. In one of the columns the wastewater pH was reduced by dosing with HCl. The two filtration rates were 4.5 and 5 m^3/m^2h. Wastewater was kept with the chemicals for different times from 2 to 15 min before it was fed to the column. The research lasted about 1 mo. During the work of the system, breakthrough in the bed was often observed in the initial phases of the filtration cycle, the length of which was from only 4 to 8 h. The extent of color and COD removal according to wastewater pH after the process is as follows:

Wastewater pH	4.5 to 6.0	6.0 to 7.0	7.0 to 8.0
Color removal--%	40 to 50	40 to 50	20 to 30
COD removal--%	average 60	average 60	30 to 40 .

No mention has been made of results of determination in samples collected during periods in which coagulation took place partially above the bed. The filtration cycles were short because the bed parameters were inappropriate and the filtration rate was too great.

In system B, the bed medium was changed and different filtration rates were used. The granulation compositions of individual bed layers were:

layer 0.15 m high--gravel d = 6 to 8 mm
layer 0.25 m high--gravel d = 3 to 5 mm
layer 1.15 m high--sand d = 1 to 2 mm
layer 0.20 m high--sand d = 0.4 to 0.8 mm

A coagulant dose of 200 to 230 mg/l of alum and a filtration rate with two ranges, 4.5 to 5.0 and 3.0 to 3.5 m^3/m^2h, were used. The remaining parameters were unchanged from system A. The removal of color and other indicators was the same as in the previous research. The filtration cycle at a rate of 4.5 to 5.0 m^3/m^2h was likewise 4 to 8 h. The results obtained were unsatisfactory because of the large amount of suspended solids in the effluent and the short filtration cycle. Decreasing the filtration rate to 3.0 to 3.5 m^3/m^2h caused a prolongation of the cycle to 8 to 12 h.

In system C, the composition of the filtration media and the granulation of individual layers were as follows:

layer 0.15 m high--gravel d = 2 to 4 mm
layer 1.5 m high--gravel d = 1.2 to 2 mm
layer 0.15 m high--sand d = 0.4 to 0.8 mm

The average coagulant dose was 180 to 200 mg/l of alum. The filtration rate decreased to 2 m^3/m^2h. The time the wastewater was retained after the addition of chemicals was about 4 min. The process was conducted simultaneously in two columns. The pH of the wastewater fed to one of the columns was decreased with hydrochloric acid. The average filtration cycle to the moment of penetration of the bed was about 24 h.

The results were divided into two groups according to the wastewater pH after coagulation.

The average results from 16 24-h periods of plant operation for pH higher than 6.8 are given in table 7-4, and the average results from 24 24-h periods for pH lower than 6.8 are given in table 7-5. The pollutant removal obtained is satisfactory. The removal of biodegradable organic substances was considerable, totaling about 80 percent. Organic compounds that decompose with difficulty by biochemical means and are determined by COD were also removed. In these investigations, the positive influence of decrease in wastewater pH during coagulation was confirmed, especially on color removal from wastewater.

Influence of preliminary oxidation--Wastewater fed to system C was oxidized using NaOCl in a dose of 10 to 14 mg of Cl_2/l. The contact time of the oxidizer with the wastewater before the coagulant was fed in was 15 min (tables 7-6 and 7-7). The results obtained in this series were compared with the results of previous investigations in order to determine the influence of oxidation, especially on the removal of color from wastewater. A 10 to 20 percent increase in color removal was found after preliminary oxidation of wastewater. The influence of decrease in wastewater pH on the treatment results was similar to that apparent in the previous series of investigations. With oxidation, total color removal (70 percent) was greater. The amount of residual oxidant was from 0 to 2 mg of Cl/l.

Influence of change in concentration of pollutants fed to the coagulation process--During the period of research, a change occurred in the loading of the activated sludge system. This influenced the change in the quality of the wastewater. The process parameters are the same as in the previous series. The values obtained are presented in tables 7-8 and 7-9. The pollutant removal with an unchanged coagulant dose was the same as in the previous series. The quantities of pollutants removed for a unit dose of coagulant increased considerably.

System D was the last of the continuous pilot investigations in 1976. The composition filter media and their granulation were as follows:

layer 0.4 m high--gravel d = 3 to 6 mm
layer 1.9 m high--sand d = 1.2 to 2 mm
layer 0.2 m high--sand d = 0.4 to 0.8 mm

The filtration rates increased to 3 m^3/m^2h. A dose of 250 to 270 mg/l of alum was used. The filtration cycle lasted about 24 h. The final loss of pressure was about 5 m of H_2O. The average results from the initial 2-wk period of operation of the system are presented in table 7-10. Over 50 percent removal of COD, BOD_5, and suspended solids was obtained. Colored substances in the wastewater were removed to a considerably lesser degree. The percentage of anionic detergent removal was about 50 percent with an initial content of less than 1 mg/l. The nonionic detergent content in the wastewater before the process was about 10 mg/l, and the removal percentage during coagulation was over 50 percent.

A further series of investigations was performed in the same system using the same parameters but with the wastewater pH decreased by means of hydrochloric acid. After coagulation, the wastewater was oxidized with a dose of 15 to 20 mg of Cl_2/l of NaOCl, and then filtered through an anthracite-sand bed at flow rate of 8 m^3/m^2h. The results in this series are given in table 7-11.

Decrease in wastewater pH from 7.3 to 6.8 caused a particularly significant increase in removal of yellow color measured by an extinction of 400 nm (tables 7-10 and 7-11). Oxidation of wastewater after coagulation with repeated filtration caused an increase in removal percentages of all the first indicators. Color removal at 550 nm increased by 62 percentage points, and at 400 nm by 21 percentage points. The content of residual oxidant was from 4 to 8 mg of Cl_2/l.

Technological System of Conventional Coagulation in the Reactor with Suspended Flocs--

Preliminary investigations were carried out on biologically treated wastewater with parameters approximate to those given in table 7-4. In this research the influence of flow rate in the reactor on the coagulant effects was determined. The flow rates were 5, 3, 2, and 1 m^3/m^2h. Doses of 180 to 200 mg/l of alum were applied. The investigations at one flow rate lasted about 2 wk. Analysis of the results showed that the flow rate should not exceed 3 m^3/m^2h. Further investigations were always carried out at a rate of 3 m^3/m^2h.

After coagulation the wastewater passed to an anthracite-sand filter with the following granulation:

layer 0.5 m anthracite--d = 0.8 to 1.6 mm
layer 0.5 m sand--d = 0.4 to 0.8 mm

The filtration rate was about $6^3/m^2h$. The average values of the results of work of the system in the first series of investigations are given in table 7-12. The results show that the effectiveness of pollutant removal in the coagulation process in the reactor itself and in a system composed of reactor and filter was very close.

After the proportion of industrial wastewater in the combined mixture fed to the activated sludge was increased, the quality of wastewater fed to the coagulation process worsened. This caused a considerable decrease in the effectiveness of coagulation. Tests to increase the coagulant dose rectified the situation. In further research, a dose of 270 to 300 mg/l of alum was used. The average values obtained from the second series for this alum dose are given in table 7-13. From a comparison of the removal effects after the reactor with suspended sludge and in the reactor supplemented by a filter, it can be stated that in this series the filtration process aids in pollutant removal.

Further investigations on coagulation in a reactor were carried out in 1976. During tests at a rate of 3 m^3/m^2h and with a dose of 200 mg/l of alum, a large amount of suspended solids floated on the surface of the reactor. This phenomenon was caused by tiny bubbles of gas floating above the surface of the reactor. Decreasing the pH and initial oxidation intensified the effects of suspended solids flotation. Decreasing the flow rate to 2 m^3/m^2h did not eliminate this phenomenon.

Summary of Investigations on Coagulation

The course of the conventional coagulation process carried out in the reactor with the layer of suspended flocs depends on the effectiveness of previous biological treatment of the wastewater. With a small amount of suspended solids in the inflow and with low parameters of other pollutants, the process conducted in this way gives good results. Changes toward higher concentrations decrease the removal effected by the process of coagulation itself. An important factor in pollutant removal in this case is filtration. Changes in pollutants can make it impossible to carry out the process as a result of the natural flotation of the sludge, which is presumably caused by the presence of calcium carbonate in the suspended solids.

The process of removing pollutants by the contact coagulation method can be regarded as appropriate, effective, and economical for treatment of this type of waste. Irrespective of the effectiveness of previous biological treatment with activated sludge, removal of refractory pollutants from wastewater was effective. It was found that reduction in wastewater pH and additional oxidation aided in pollutant removal during this process. The filtration rate can be raised by increasing the depth of the bed so as to maintain adequate reaction time. The bed should be so constructed that there is no strong mixing of individual bed layers with different granulation.

CONCLUSIONS

The following conclusions can be drawn from the laboratory and pilot investigations:

1. Aluminum salts should be used for coagulation of wastewater, since the use of ferric salts causes secondary wastewater color.
2. Before the coagulation process, preliminary treatment is necessary for pH control and efficient removal of organics in the activated sludge process so that secondary pollution of the wastewater by aluminum compounds developing in the solution does not occur.
3. Decrease in pH produces better removal for pollutants dissolved in water.
4. Preliminary oxidation before the coagulation process increases the removal of color and nonionic detergents.
5. The method of coagulation with simultaneous filtration lends itself more to coagulation of biologically treated wastewater than the conventional coagulation performed in a reactor with suspended flocs.

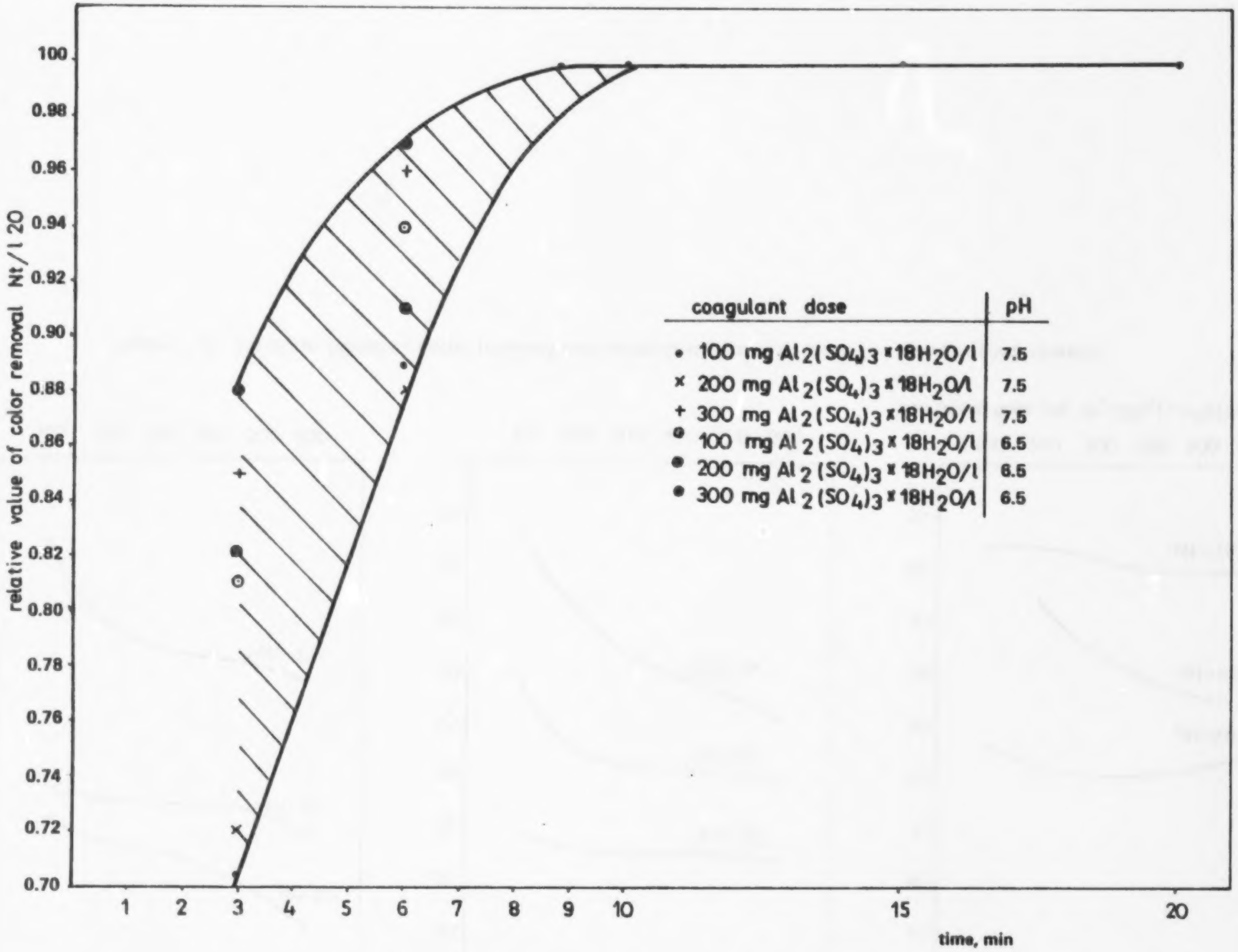


Figure 7-1. The relative value of color removal according to coagulation time.

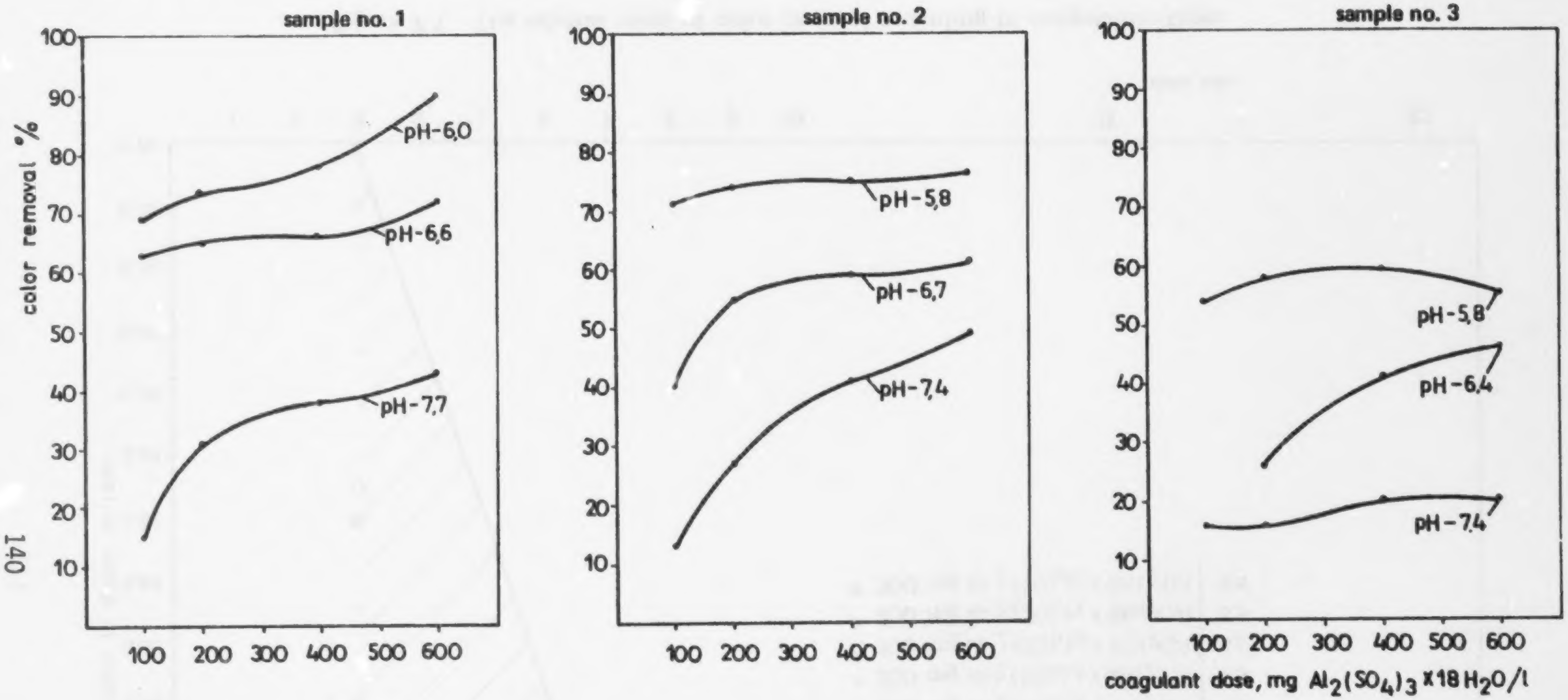


Figure 7-2. Relation between color removal and coagulant dose for three pH values of wastewater.

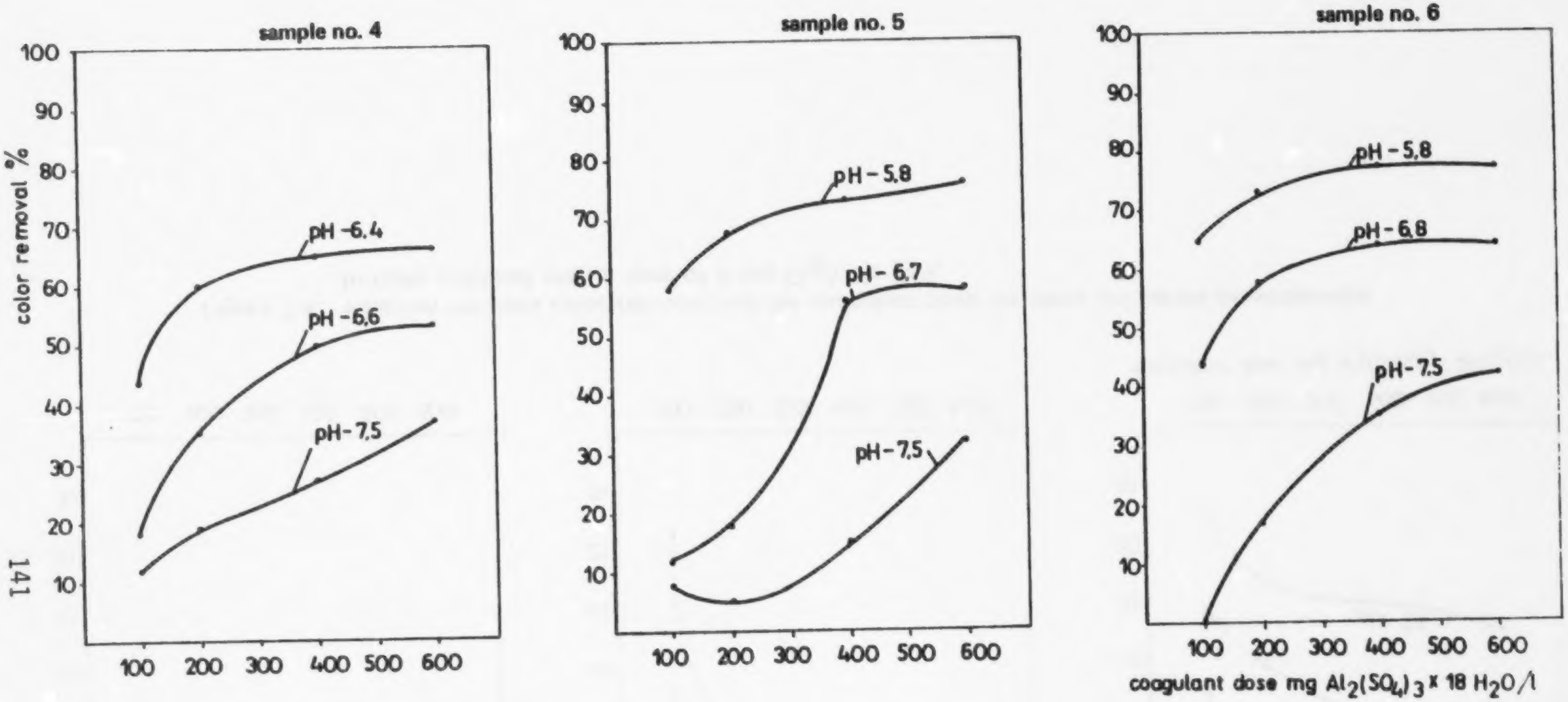


Figure 7-3. Relation between color removal and coagulant dose for three pH values of wastewater.

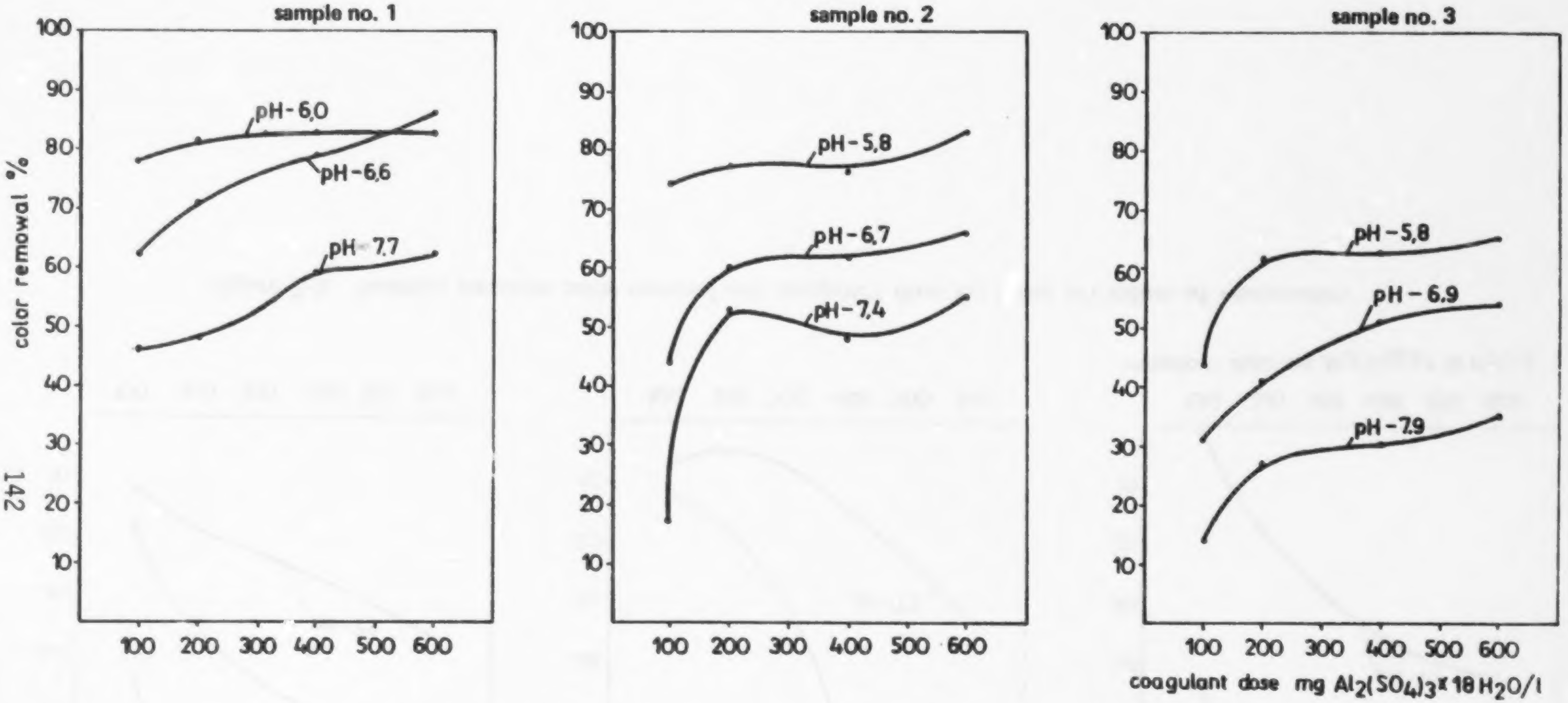


Figure 7-4. Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 8 mg Cl_2/l Na OCl.

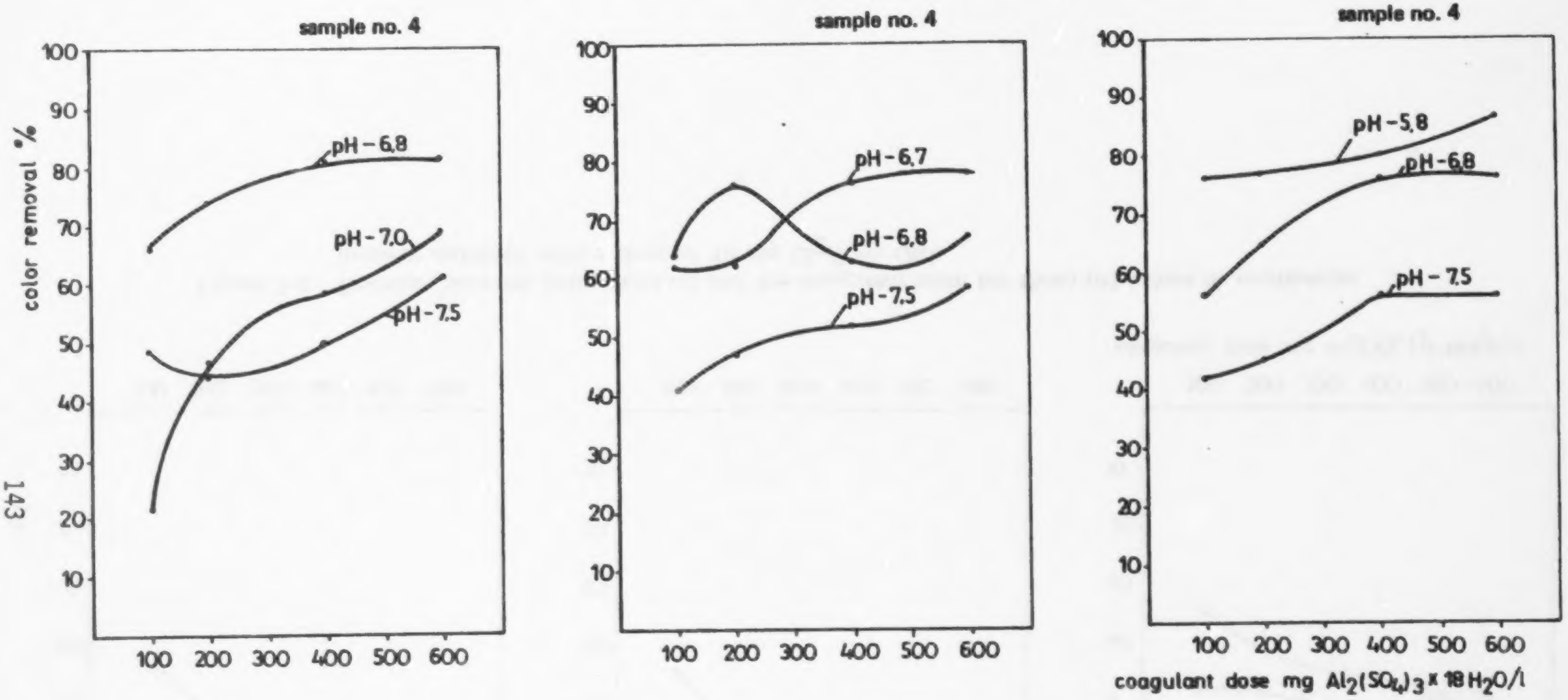


Figure 7-5. Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 8 mg Cl_2/l Na OCl.

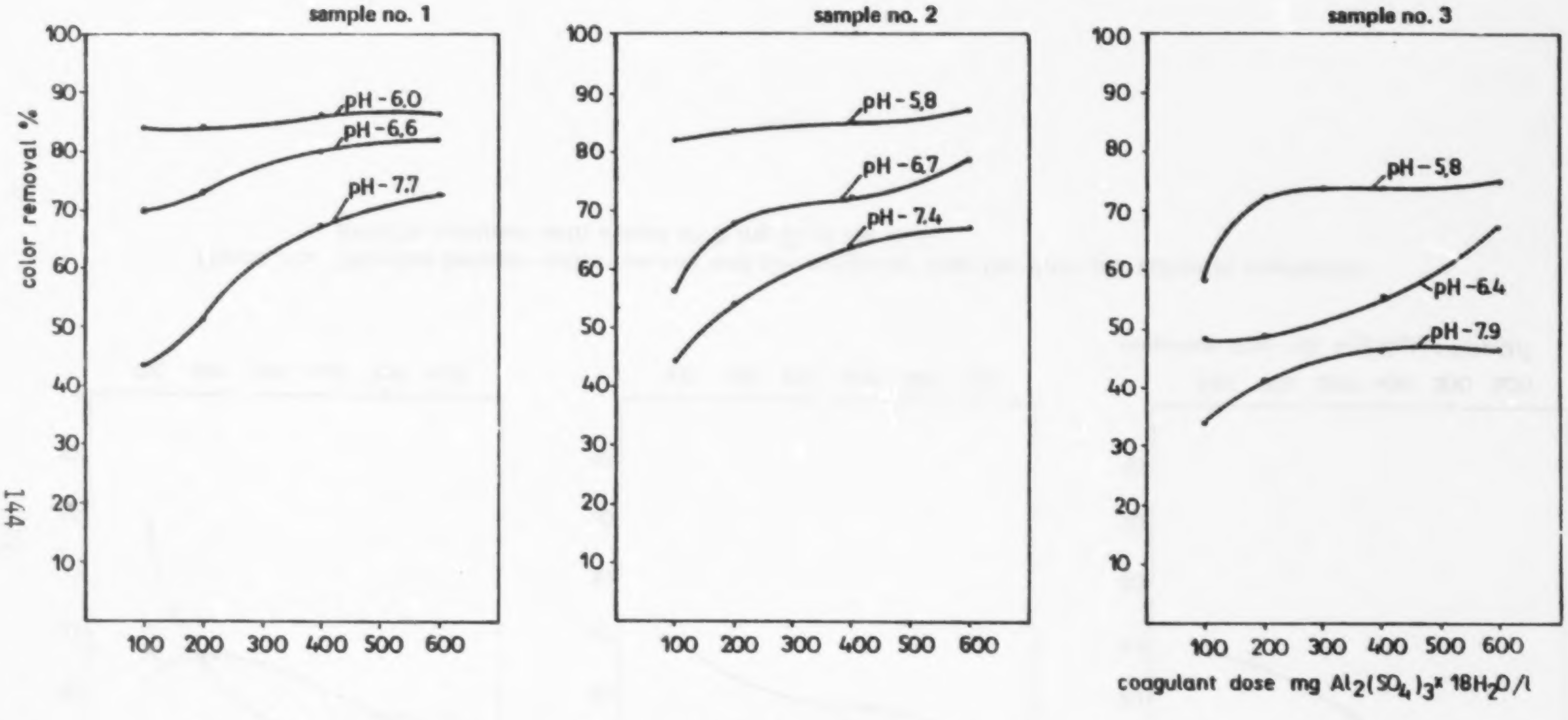


Figure 7-6. Relation between color removal and the coagulant dose for three pH values in wastewater initially oxidized with a dose of 16 mg Cl_2/l Na OCl.

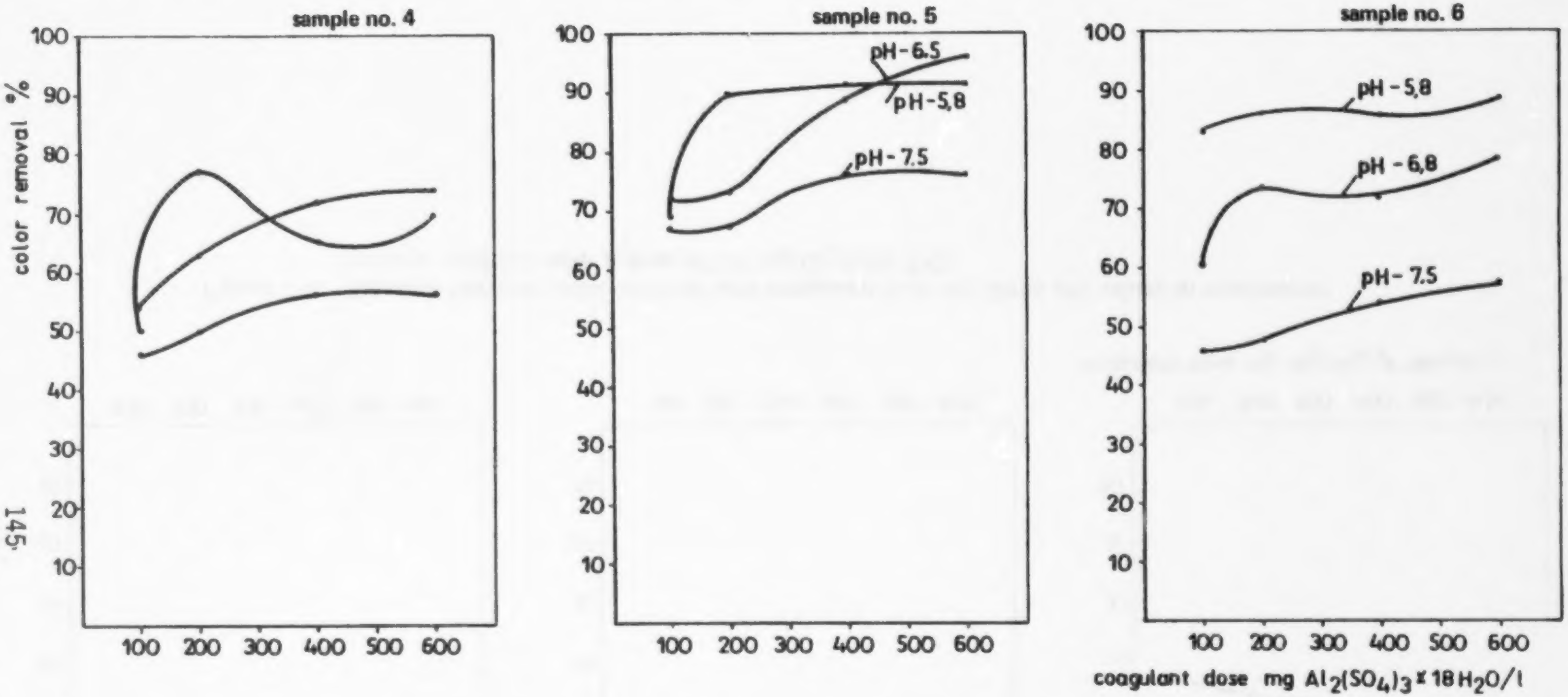


Figure 7-7. Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 16 mg Cl_2/l Na OCl.

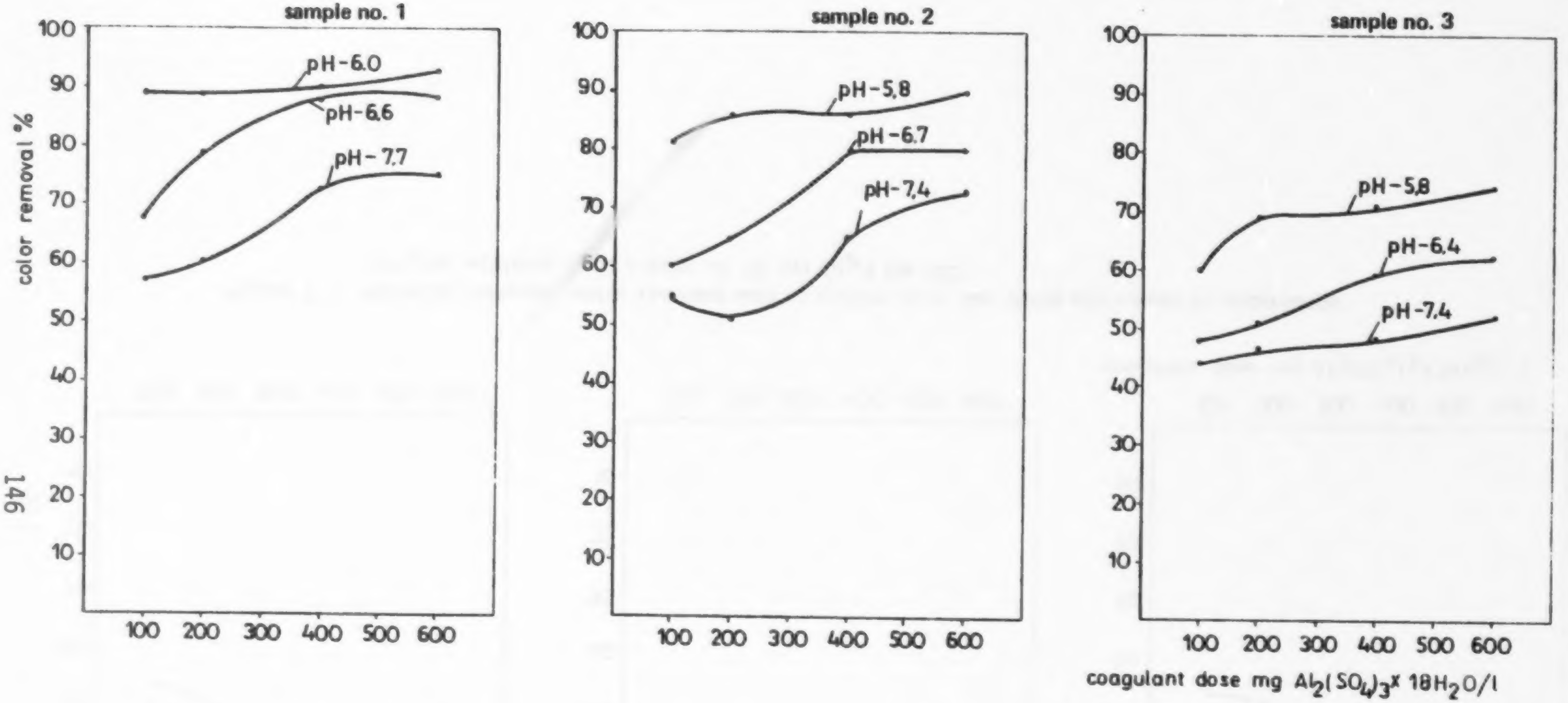


Figure 7-8. Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 24 mg Cl_2/l Na OCl.

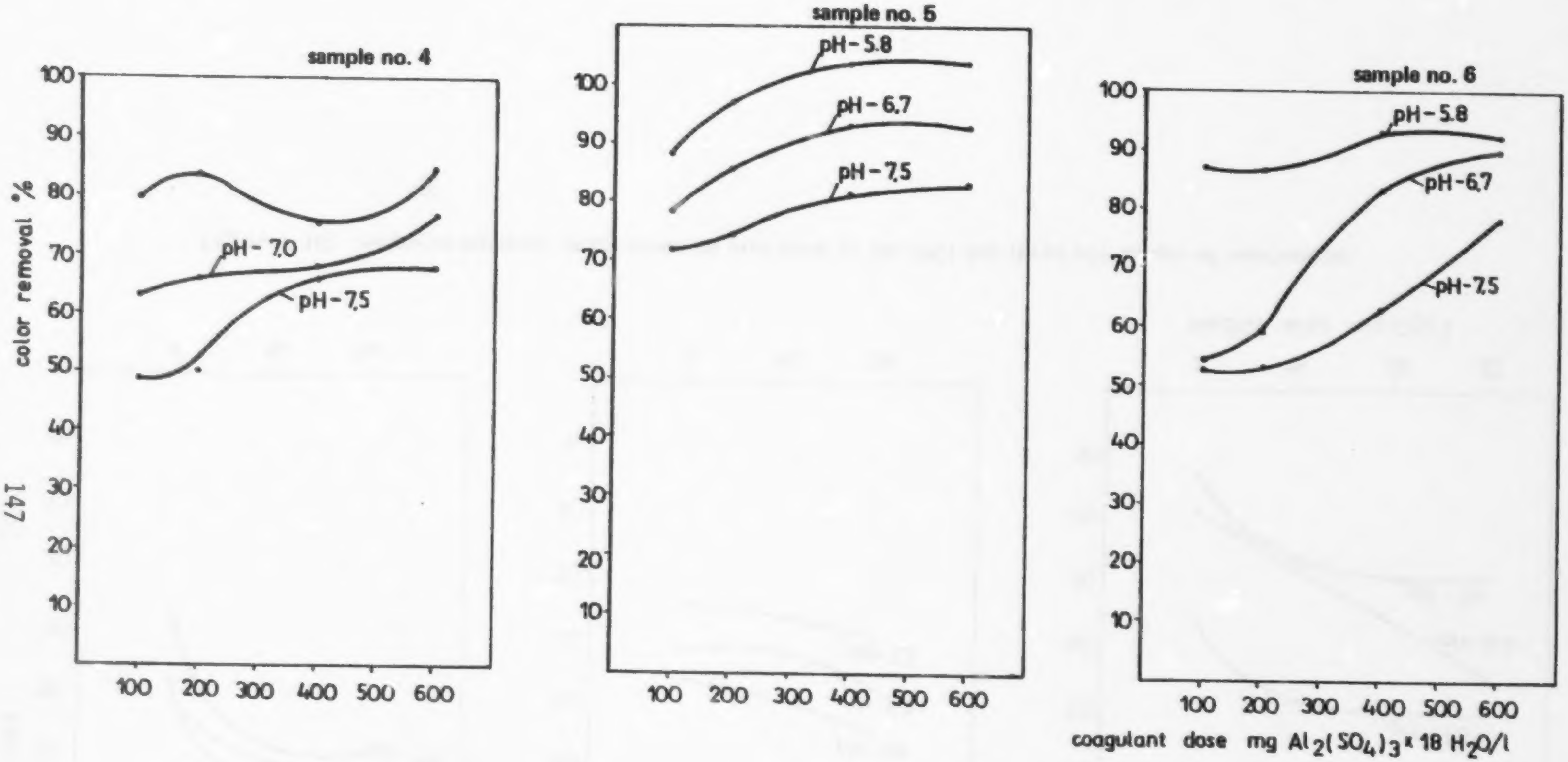


Figure 7-9. Relation between color removal and coagulant dose for three pH values in wastewater initially oxidized with a dose of 24 mg Cl_2/l Na OCl.

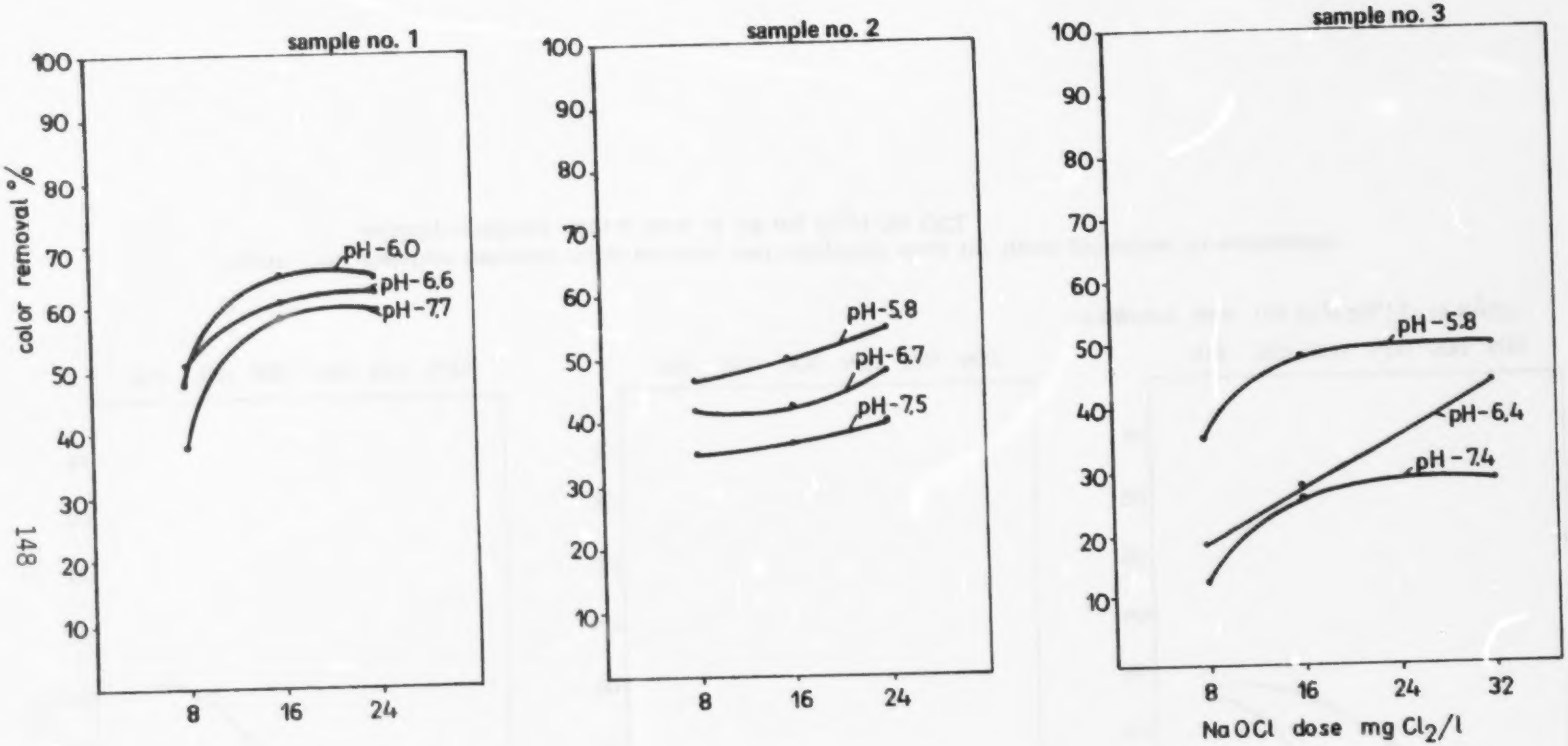


Figure 7-10. Relation between color removal and dose of Na OCl for three pH values of wastewater.

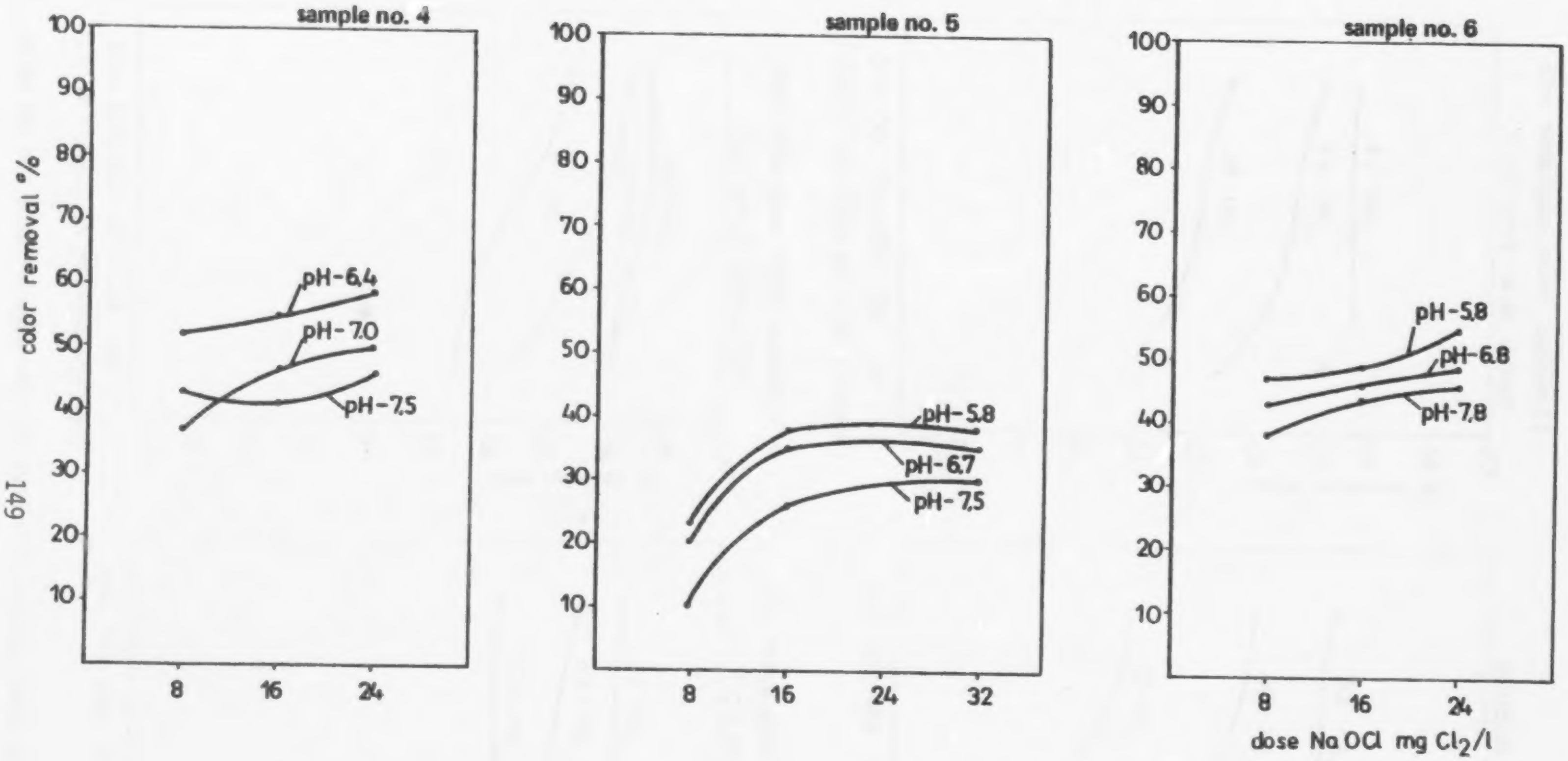
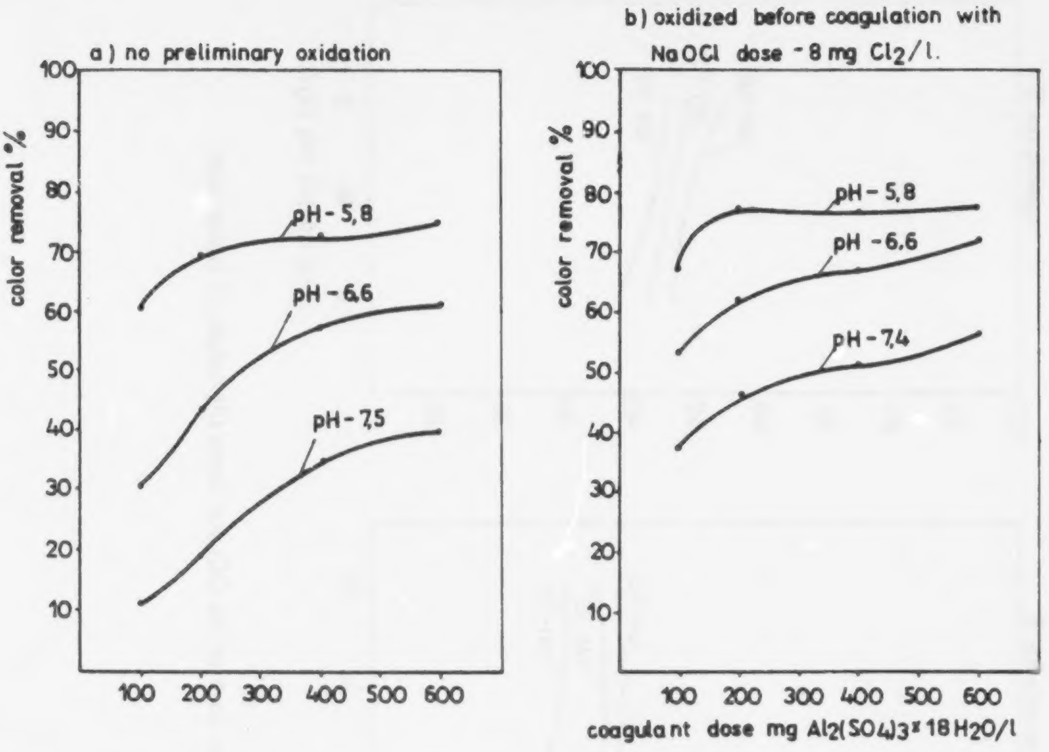
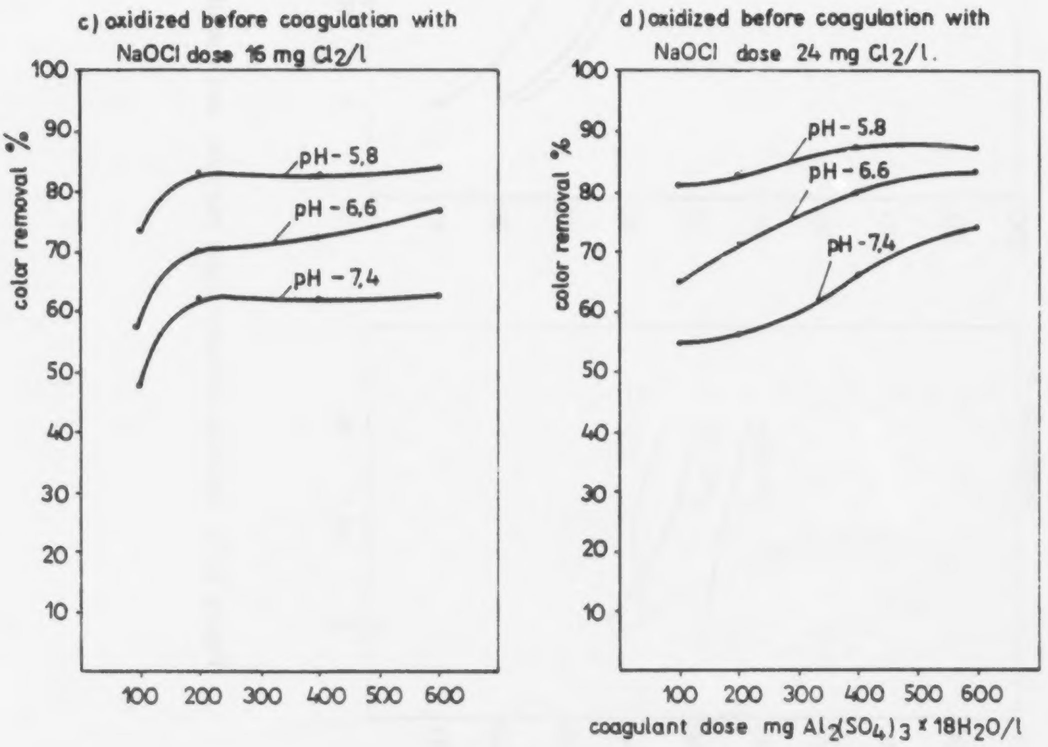


Figure 7-11. Relation between color removal and coagulant dose of Na OCl for three pH values of wastewater.


a) no preliminary oxidation

b) oxidized before coagulation with NaOCl dose - 8 mg Cl_2/l.


c) oxidized before coagulation with NaOCl dose 16 mg Cl_2/l

d) oxidized before coagulation with NaOCl dose 24 mg Cl_2/l.

Figure 7-12. Average color removal in relation to the coagulant dose and pH value.

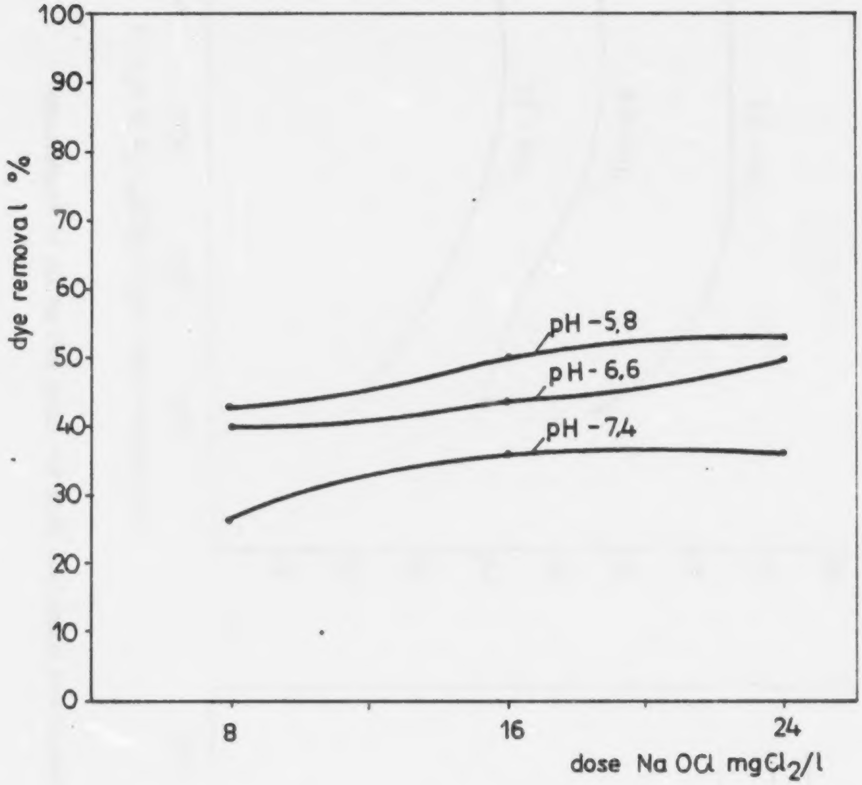


Figure 7-13. Average color removal during the preliminary oxidation with Na OCl in relation to pH values.

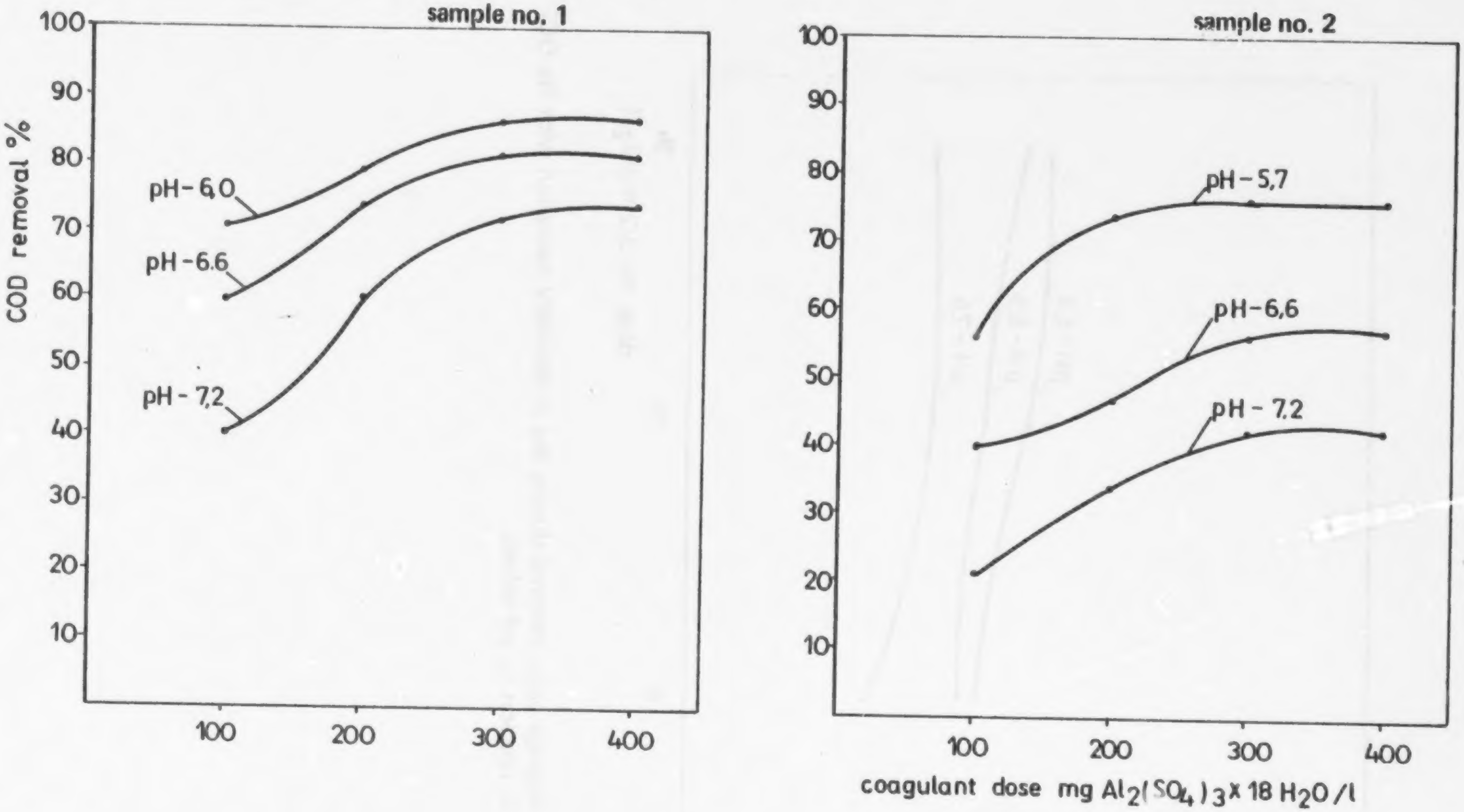


Figure 7-14. Relation between COD removal and coagulant dose for three pH values in wastewater.

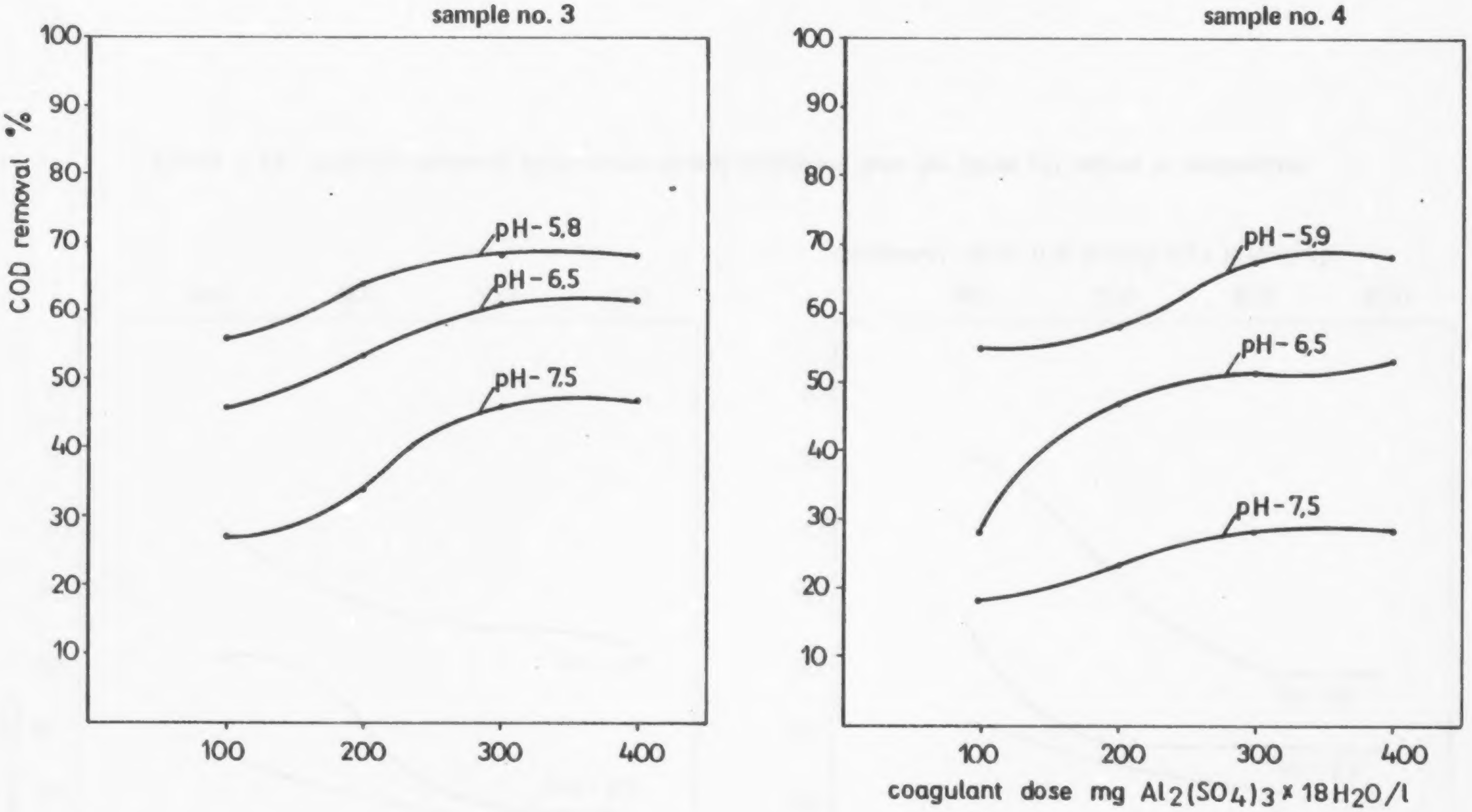


Figure 7-15. Relation between COD removal and coagulant dose for three pH values in wastewater.

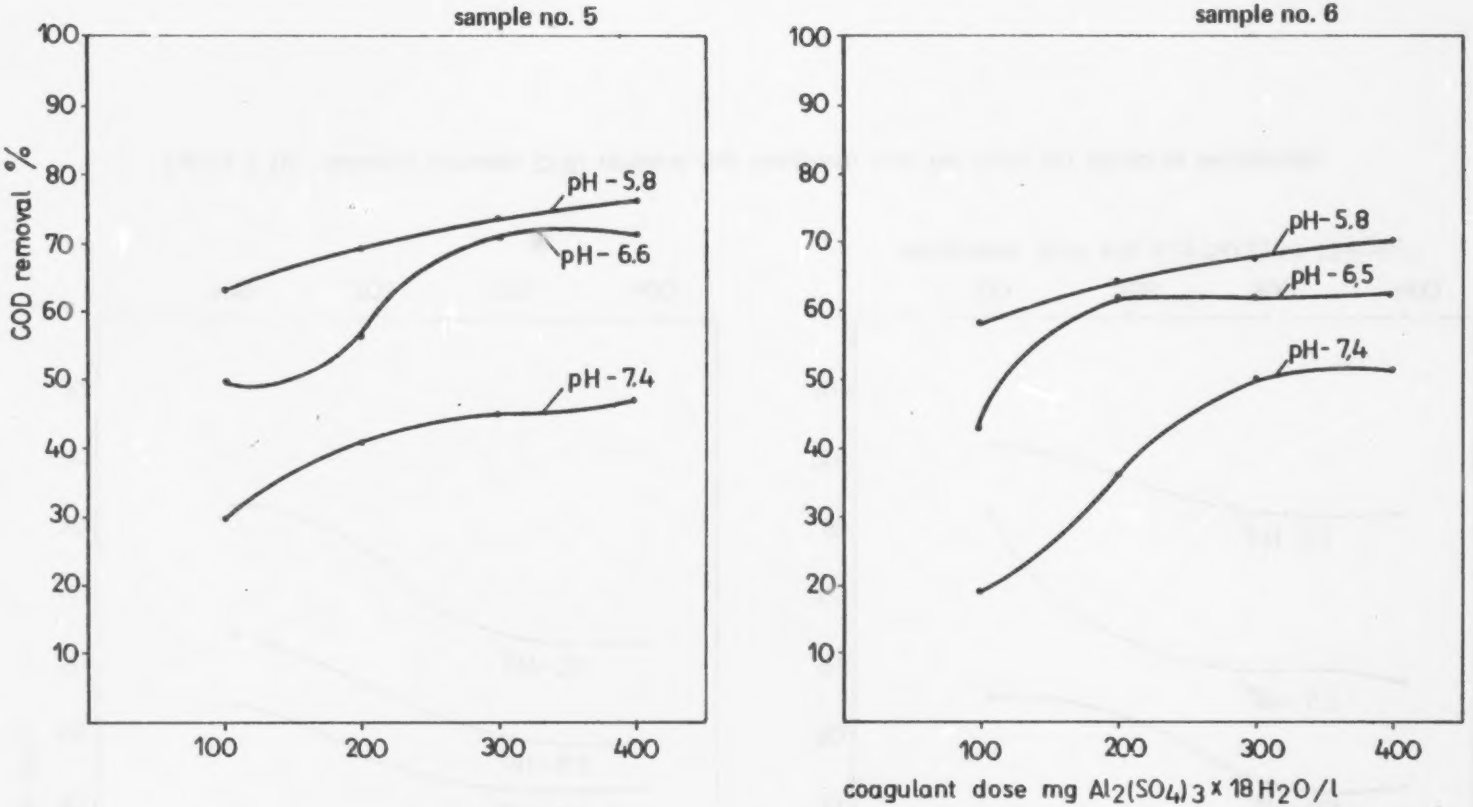


Figure 7-16. Relation between COD removal and coagulant dose for three pH values in wastewater.

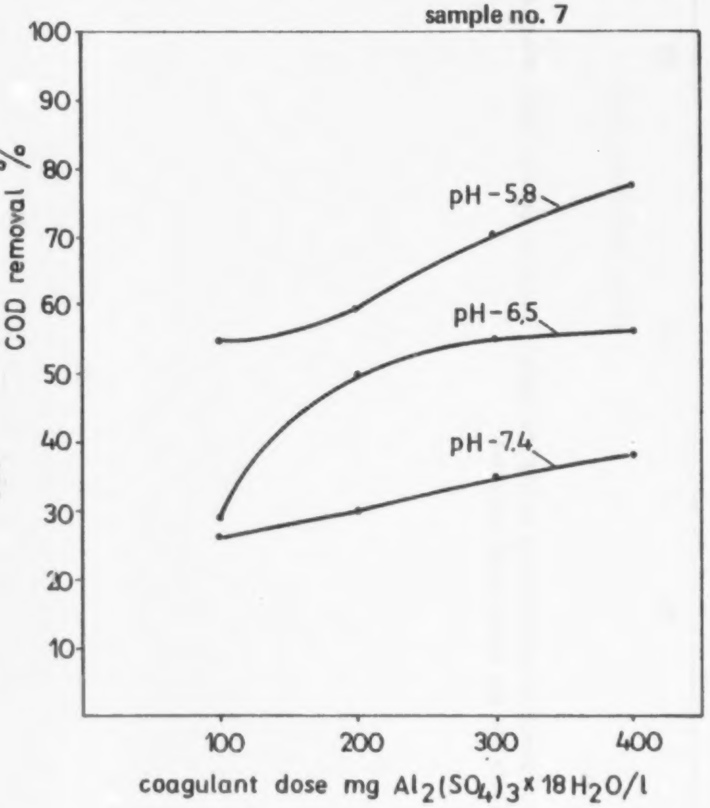


Figure 7-17. Relation between COD removal and coagulant dose for three pH values in wastewater.

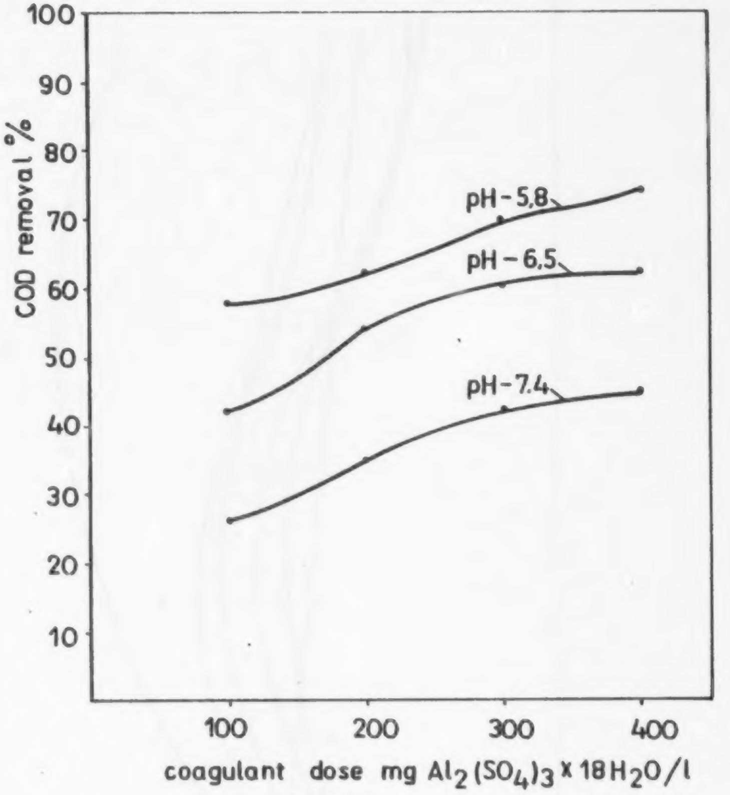


Figure 7-18. Average COD removal in relation to coagulant and pH value.

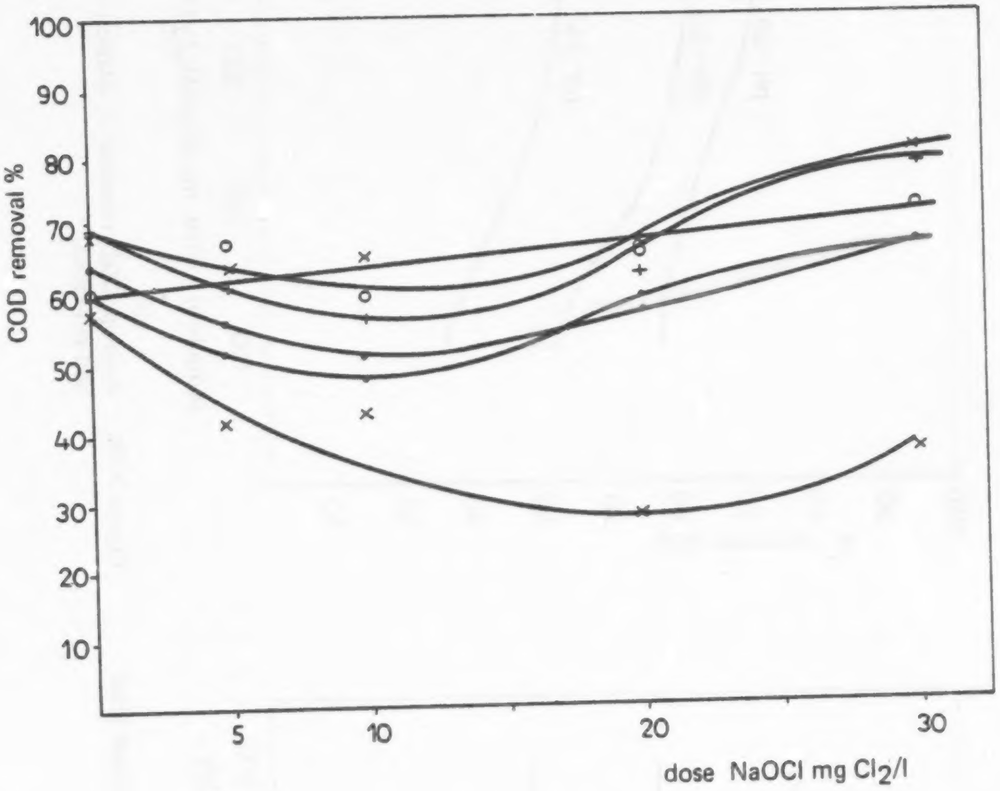


Figure 7-19. **Influence of preliminary oxidation before coagulation on COD removal. Tests for six wastewater samples.**

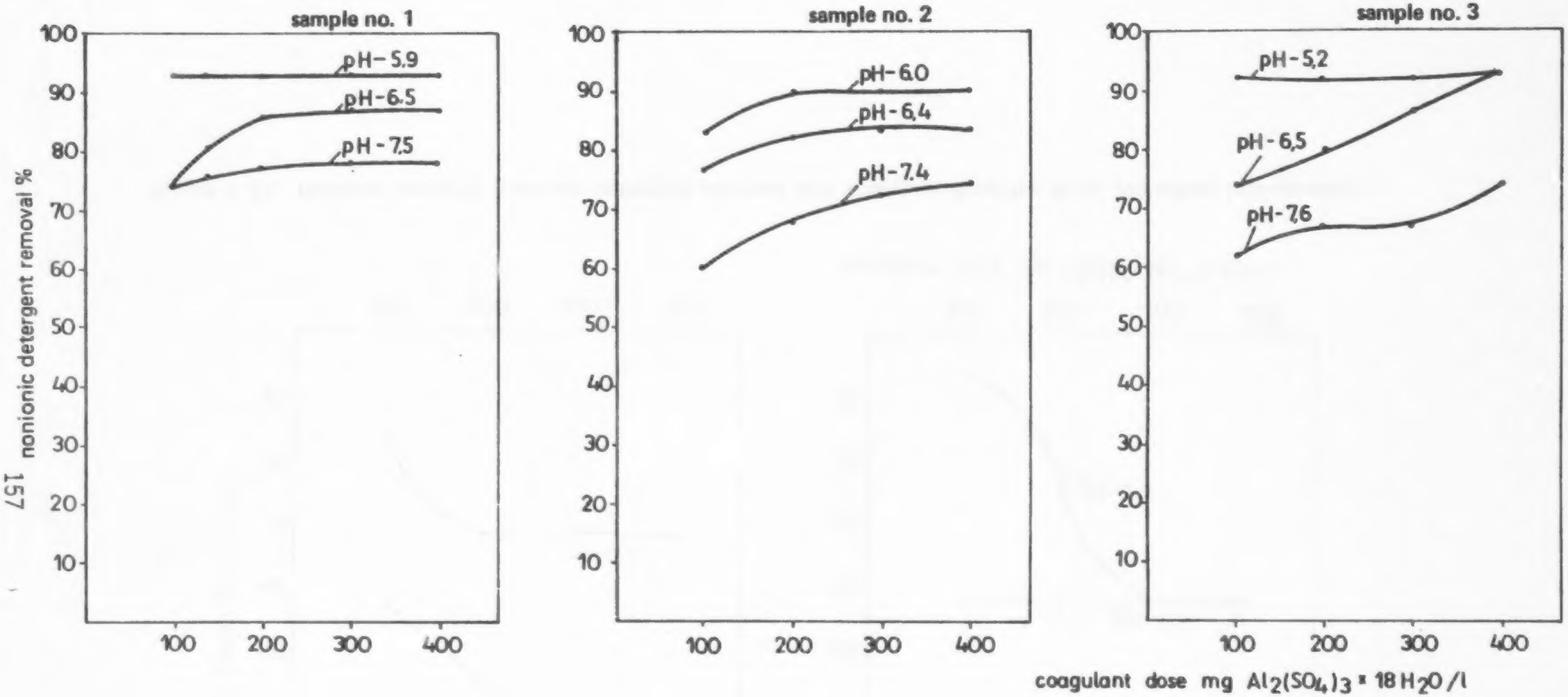


Figure 7-20. Relation between nonionic detergent removal and coagulant dose for three pH values in wastewater.

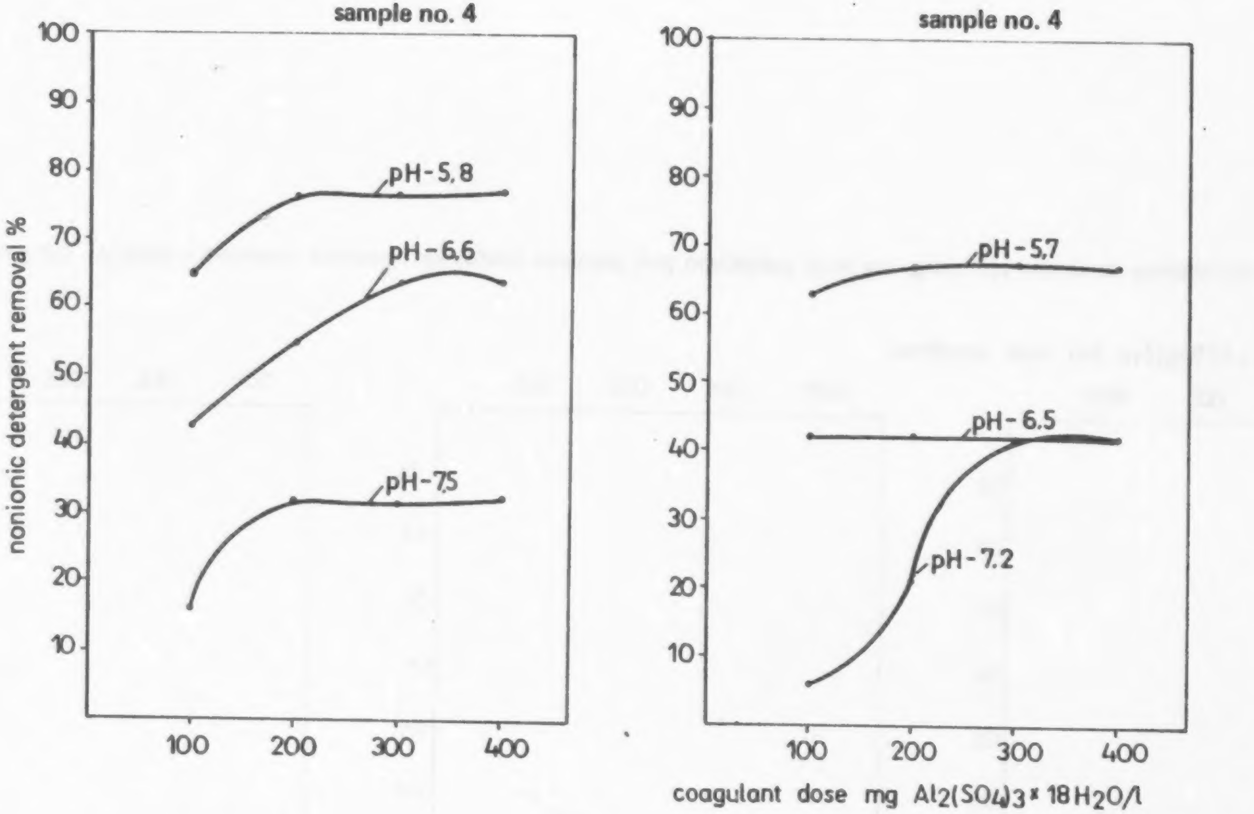


Figure 7-21. Relation between nonionic detergent removal and coagulant dose for three pH values in wastewater.

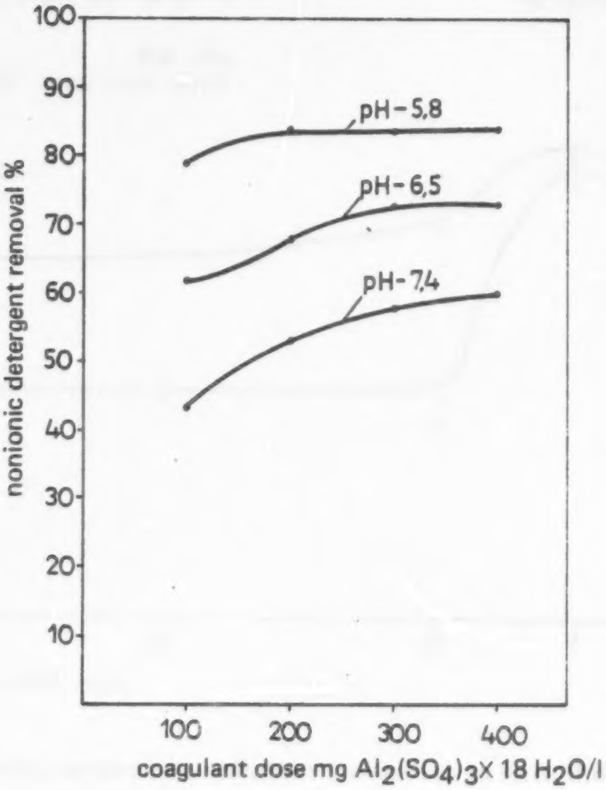


Figure 7-22. Average removal of nonionic detergents in relation to the coagulant dose and the pH values in wastewater.

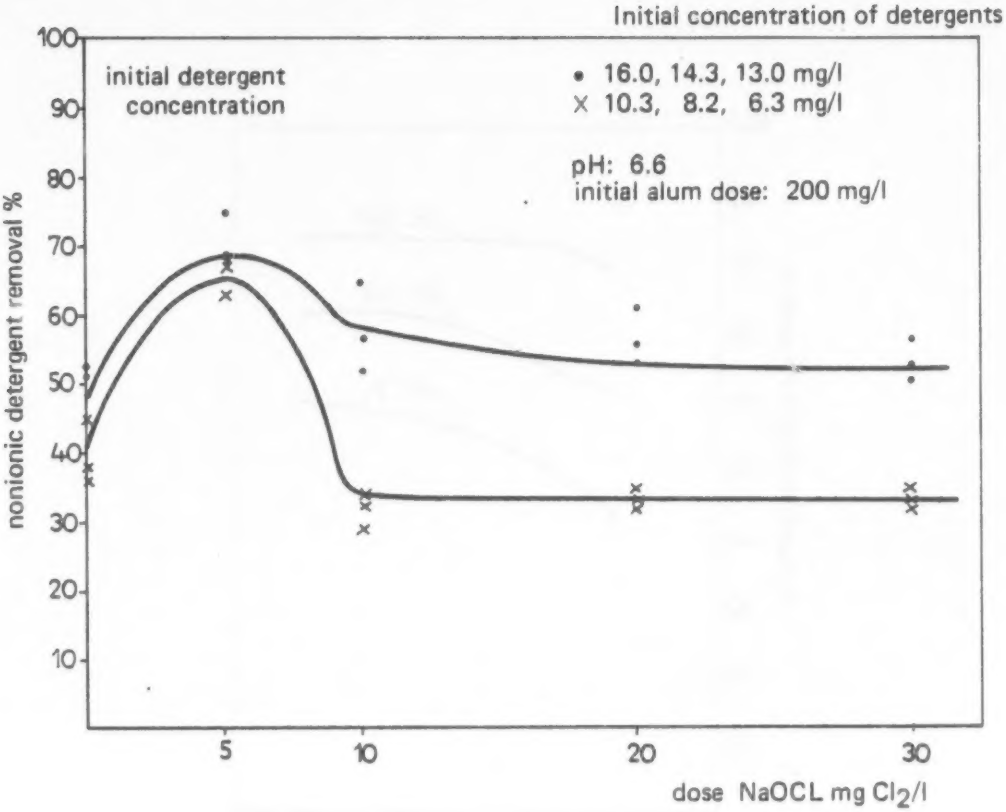


Figure 7-23. Influence of preliminary oxidation on nonionic detergent removal in wastewater after coagulation.

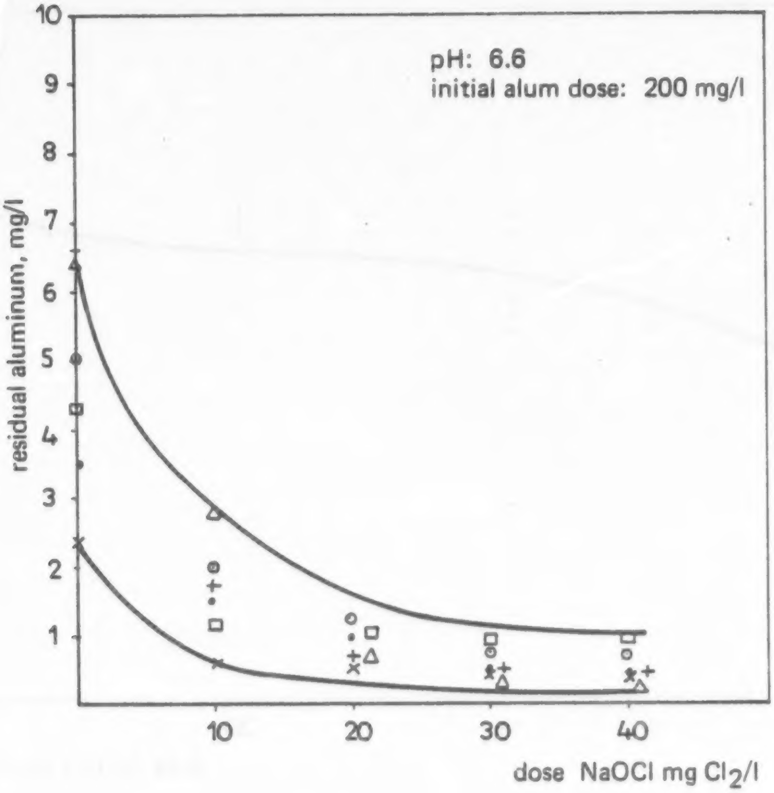


Figure 7-24. Influence of oxidation with NaOCl on removal of residual aluminum from coagulated wastewater.

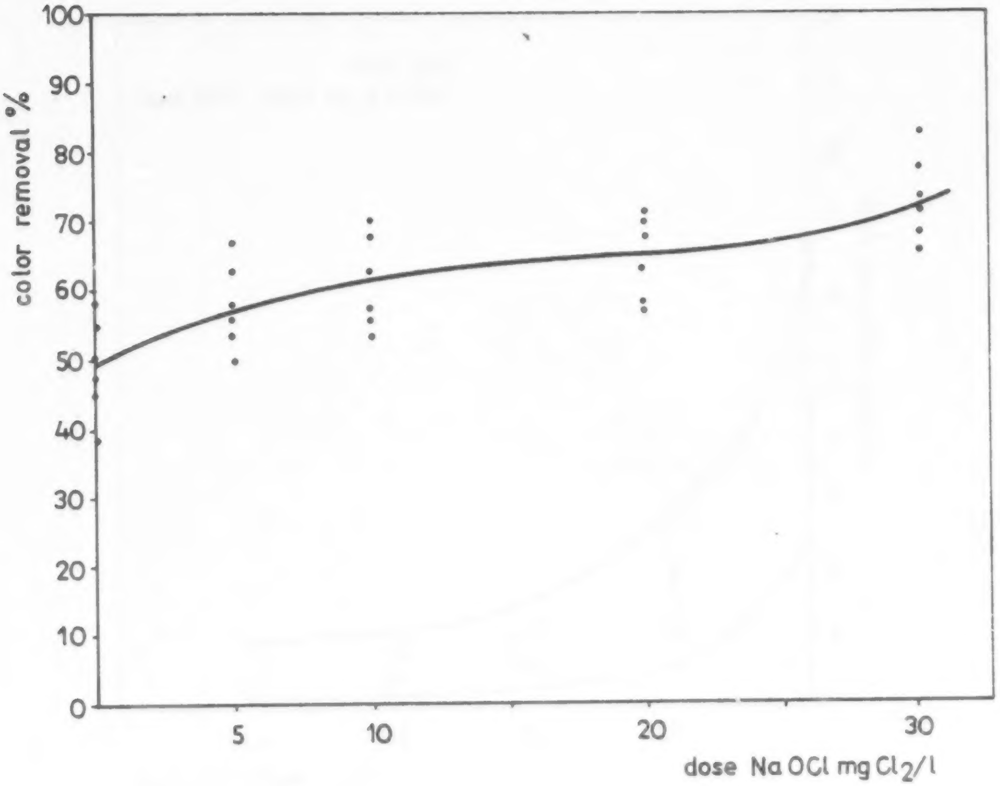


Figure 7-25. Relation between the removal of color measured spectrophotometrically at λ = 400 nm and the dose of NaOCl added before coagulation with 200 mg $Al_2(SO_4)_3 \times 18\ H_2O$/l.

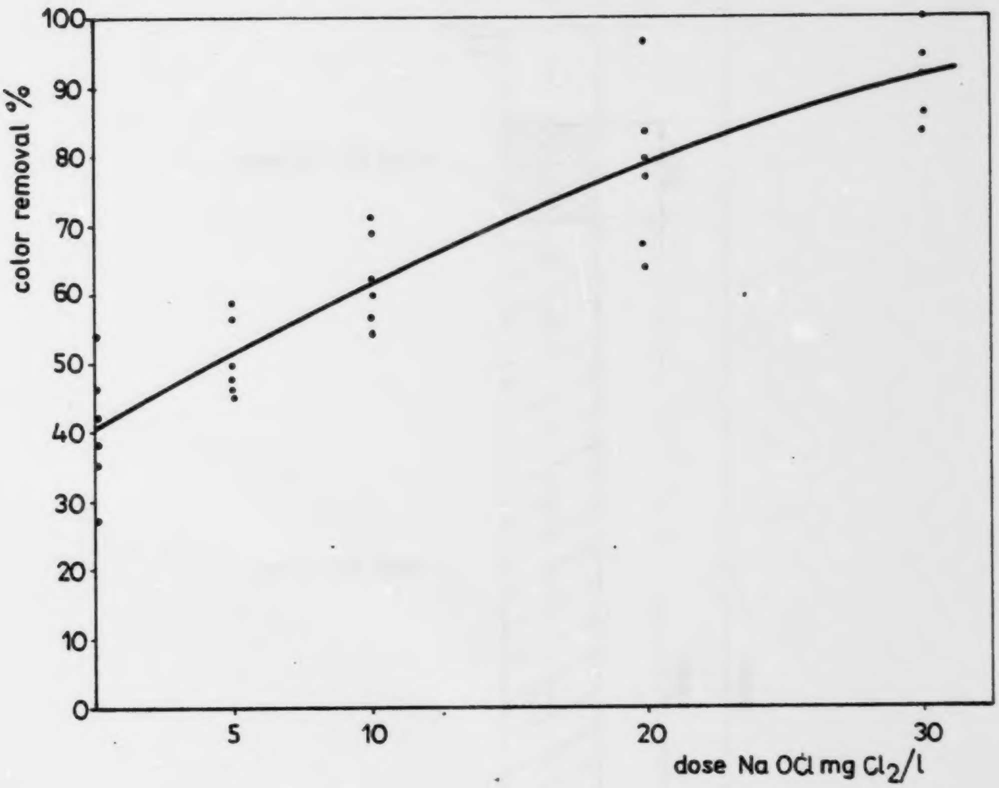


Figure 7-26. Relation between the removal of color measured spectrophotometrically at the λ = 550 nm and the dose of NaOCl added before coagulation with 200 mg $Al_2(SO_4)_3 \times 18\ H_2O$/l.

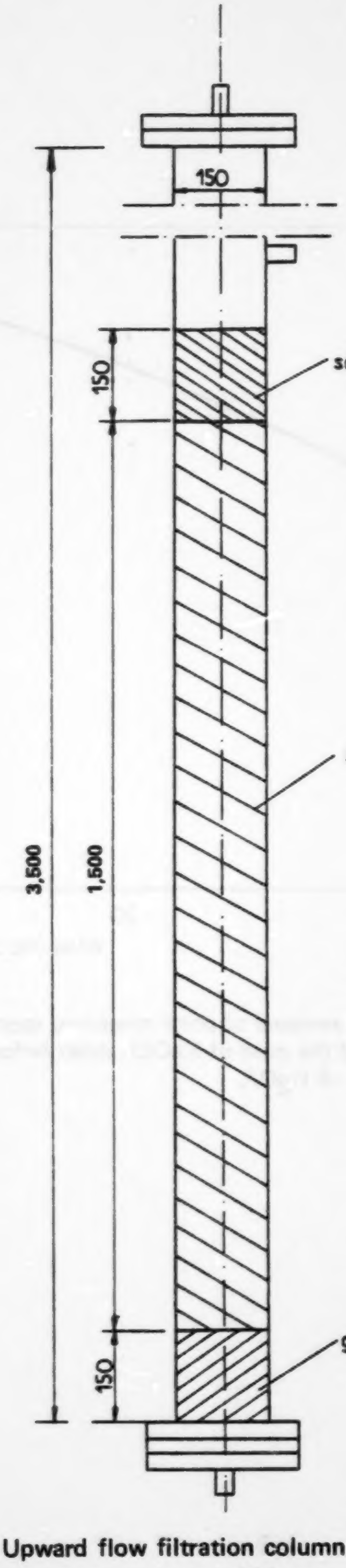

150
150
sand 0,4 - 0,8 mm
sand 1,2 - 2 mm
3,500
1,500
150
gravel 2 - 4 mm

Figure 7-27. Upward flow filtration column used for contact coagulation.

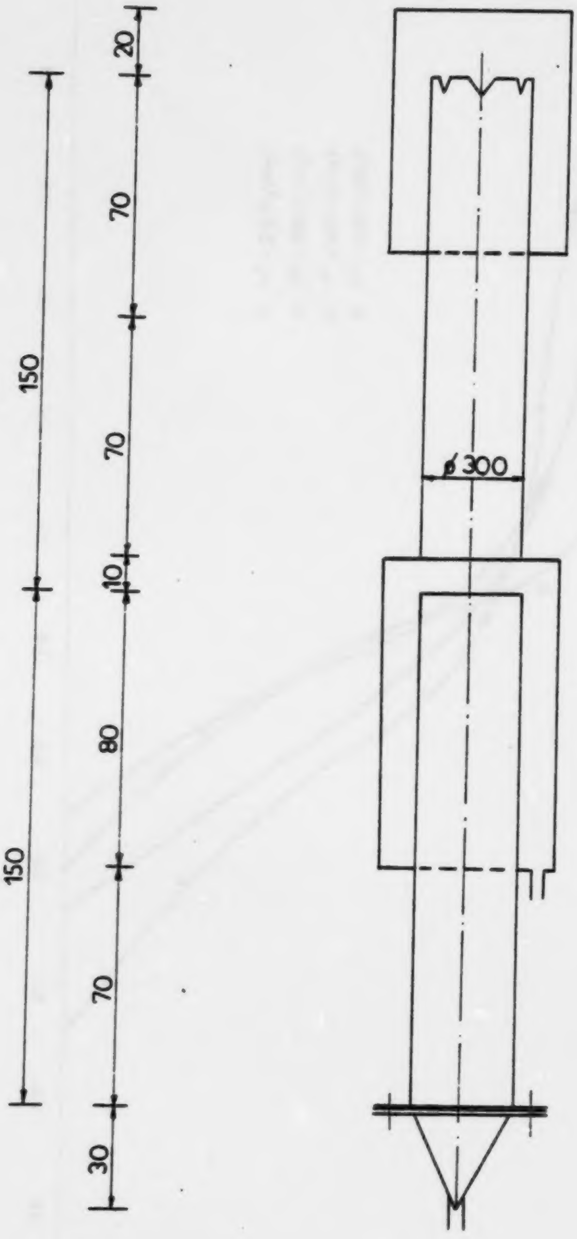

20
70
70
10
80
70
30
150
150
ø300

Figure 7-28. Coagulation reactor with suspended flocs.

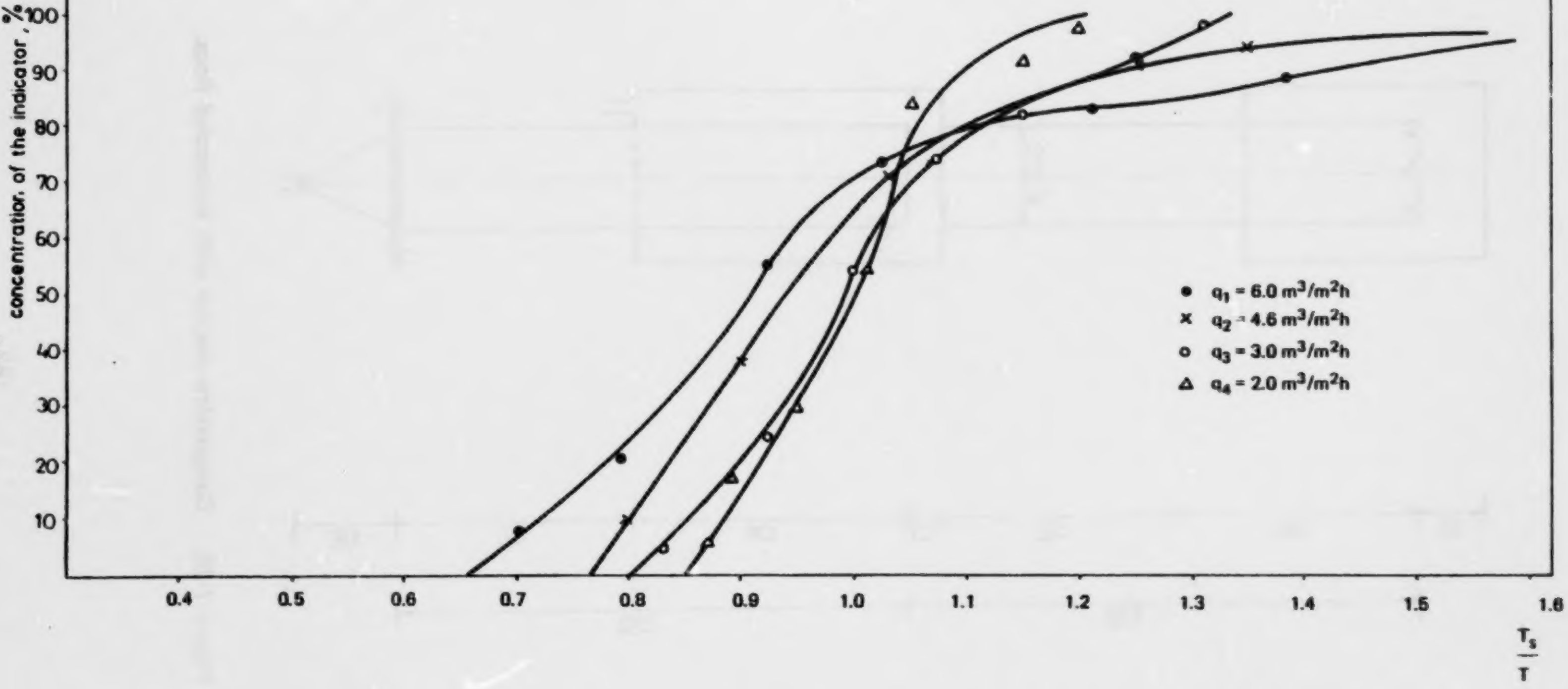


Figure 7-29. Flow time spectrum in filtration columns.

Table 7-1. Percent content of particular dye groups in total consumption of dyes in 1975

Particular dye groups	Percent in total mass
Sulfuric	14.9
Vat	34.1
Indigosol	6.7
Reactive	3.0
Dispersed	21.0
Dispersed-vat	19
Glacial	0.01
Acidic	0.00

Table 7-2. Color removal with 8 mg of Cl_2/l

pH	Oxidation alone	Coagulation without oxidation	Coagulation with oxidation
7.4	24%	19%	45%
6.6	38%	44%	62%
5.8	42%	69%	77%

The amount of NaOCl remaining after 1 h was:

for a dose of 8 mg of Cl_2/l, 1 to 3 mg of Cl_2/l;

for a dose of 16 mg of Cl_2/l, 7 to 10 mg of Cl_2/l;

for a dose of 24 mg of Cl_2/l, 14 to 19 mg of Cl_2/l.

Table 7-3. Residual dissolved aluminum after coagulation process

$Al_2/SO_4/3^0$ 18 H_2O dose, mg/l	Wastewater samples											
	1		2		3		4		5		6	
	pH	Al, mg/l	pH	Al, mg/l	pH	Al, mg/l	pH	Al, mg/l	pH	Al, mg/l	pH	Al, mg/l
100	6.9	4.6	7.5	3.6	7.6	2.4	7.4	6.0	7.4	3.9	7.2	5.8
200	6.6	5.0	7.1	2.8	7.0	2.4	6.9	6.0	7.0	3,5	6.7	5.0
300	6.2	5.0	6.8	1.6	6,6	2,6	6,5	7,2	6,7	4,2	6,2	5,3
400	5.6	8.2	6.5	2.4	6.2	2.9	6,1	7.4	6.0	4,7	5.6	5,3

Table 7-4. Contaminant removal during filtration with simultaneous coagulation for higher pH. (Average results based on 16 days of operation)

	Biologically treated effluent		Coagulated effluent		
Parameters	Average concentration	Standard deviation	Average concentration	Standard deviation	Removal %
pH	8.0	0.2	7.1	0.2	
Alkalinity, meq/l	7.9	2.3	5.2	2.2	
Permanganate COD, mg O_2/l	19.2	5.3	13	4.2	32
COD, mg O_2/l	78	32	34	16	56
BOD_5, mg O_2/l	15.3	3.3	3.3	2.1	78
Suspended solids, mg/l	31	12	14	9	54
Color, mg Pt/l	54	13	32	13	40
Color threshold	19:100	5:100	34:100	16:100	

Table 7-5. Contaminant removal during filtration with simultaneous coagulation for lower pH. (Average results based on 24 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Removal %
	Average concentration	Standard deviation	Average concentration	Standard deviation	
pH	7.8	0.2	6.5	0.3	
Alkalinity, meq/l	7.8	2.2	3.4	1.6	
Permanganate COD, mg O_2/l	18.5	7	9.2	3.6	50
COD, mg O_2/l	72	26	25	17	65
BOD_5, mg O_2/l	13.6	4.6	1.7	1.1	87
Suspended solids, mg/l	32	16	13	10	56
Color, mg Pt/l	57	23	21	12	60
Color threshold	19:100	6:100	60:100	30:100	

Table 7-6. Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl. (Average results based on 10 days of operation)

	Biologically treated effluent		Coagulated effluent		
Parameters	Average concentration	Standard deviation	Average concentration	Standard deviation	Removal %
pH	8.2	0.1	7.2	0.3	
Alkalinity, meq/l	10.8	1.4	8.2	1.4	
Permanganate COD, mg O_2/l	20.5	4.5	11.5	2.1	44
COD, mg O_2/l	89	13	44	10	50
Suspended solids, mg/l	25	12	11	10	56
Color, mg Pt/l	56	11	27	10	53
Color threshold	18:100	6:100	42:100	18:100	
Average light absorption, E	0.086	0.026	0.041	0.016	52

Table 7-7. Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl. (Average results based on 28 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	
pH	7.7	0.2	6.4	0.4	
Alkalinity, meq/l	8.3	3.2	3.3	1.6	
Permanganate COD, mg O_2/l	19.0	3.5	7.9	1.3	58
COD, mg O_2/l	80	29	22	6	72
Suspended solids, mg/l	50	22	9	7	82
Color, mg Pt/l	56	15	17	8	70
Color threshold	20:100	7:100	69:100	31:100	
Average light absorption, E	0.093	0.040	0.030	0.026	68

Table 7-8. Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 36 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	
pH	7.8	0.3	7.1	0.2	
Alkalinity, meq/l	16	4	14	3.7	
Permanganate COD, mg O_2/l	31	17	16	6.5	45
COD, mg O_2/l	131	32	53	10	59
Suspended solids, mg/l	60	27	18	10	70
Color, mg Pt/l	98	44	44	18	55
Color threshold	12:100	4:100	24:100	9:100	
Average light absorption, E	0.193	0.060	0.096	0.040	50

Table 7-9. Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 18 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	
pH	7.7	0.3	6.5	0.2	
Alkalinity, meq/l	11.2	5.0	5.9	4	
Permanganate COD, mg O_2/l	27	8	10.5	2.5	61
COD, mg O_2/l	120	35	37	13	69
Suspended solids, mg/l	49	31	16	9	61
Color	85	40	22	13	74
Color threshold	12:100	5:100	41:100	20:100	
Average light absorption, E	0.176	0.060	0.050	0.023	72

Table 7-10. Contaminant removal during filtration with simultaneous coagulation applied to wastewater preliminarily oxidized with NaOCl (average results based on 14 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	
pH	8.0	0.2	7.3	0.4	
Alkalinity, meq/l	8.1	1.0	5.5	0.7	
Permanganate COD, mg O_2/l	25	5	13	4	48
COD, mg O_2/l	100	27	48	12	52
BOD_5, mg O_2/l	15.5	5.0	5.8	1.6	62
Suspended solids	45	20	16	10	64
Color threshold	4:100	2:100	5.5:100	2:100	
Average light absorption, E λ = 400 nm	0.380	0.100	0.250	0.100	34
Average light absorption, E λ = 550 nm	0.190	0.070	0.120	0.040	36

Table 7-11. Contaminant removal during filtration with simultaneous coagulation, followed by oxidation with NaOCl and subsequent filtering (average results based on 14 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Coagulated, oxidized, and secondarily filtered		Removal during coagulation process, %	Total removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	Average concentration	Standard deviation		
pH	8	0.2	6.8	0.3	6.8	0.3		
Alkalinity, meq/l	8.6	1.8	4	2.2	4	2.2		
Permanganate COD, mg O_2/l	24	6	13	3	9	3	45	62
COD, mg O_2/l	100	25	40	13	30	10	60	70
Suspended solids, mg/l	20	15	10	7.5	2	1.5	50	90
Average light absorption, E λ = 400 nm	0.350	0.120	0.150	0.070	0.040	0.030	57	88
Average light absorption, E λ 550 nm	0.250	0.100	0.160	0.090	0.010	0.005	36	98

Table 7-12. Contaminant removal during coagulation in suspended flocs reactor followed by filtration (average results based on 26 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Coagulated and filtered effluent		Removal during coagulation process, %	Total removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	Average concentration	Standard deviation		
pH	7.8	0.4	7.0	0.3	7.0	0.3		
Alkalinity, meq/l	8.1	3.4	6	3	6	3		
Permanganate COD, mg O_2/l	18.5	4.5	10.2	2.6	9	2.2	44	51
COD, mg O_2/l	83	37	32	10	30	10	61	63
BOD_5, mg O_2/l	17	4	3.5	0.7	2.9	0.7	79	82
Suspended solids, mg/l	31	19	11	8	9.5	5.5	64	69
Color, mg Pt/l	55	13	28	10	28	10	49	49
Color threshold	18:100	7:100	35:100	17:100	35:100	17:100		
Average light absorption, E	0.103	0.046	0.060	0.040	0.060	0.040	41	41

Table 7-13. Contaminant removal during coagulation in suspended flocs reactor followed by filtration (average results based on 10 days of operation)

Parameters	Biologically treated effluent		Coagulated effluent		Coagulated and filtered effluent		Removal during coagulation process, %	Total removal, %
	Average concentration	Standard deviation	Average concentration	Standard deviation	Average concentration	Standard deviation		
pH	7.7	0.3	7.2	0.3	7.3	0.3		
Alkalinity, meq/l	14	4	11	4	11	4		
Permanganate COD, mg O_2/l	33	10	20	5	15	5	39	54
COD, mg O_2/l	130	50	90	30	62	28	30	55
BOD_5, mg O_2/l	22	2.5	5.8	1	4.2	1	73	78
Suspended solids, mg/l	67	30	24	18	12	10	64	82
Color, Pt/l	100	52	72	38	58	24	28	42
Color threshold	8.5:100	4:100	14:100	6:100	15:100	9:100		
Average light absorption, E	0.200	0.056	0.126	0.040	0.126	0.040	36	36

SECTION 8

ADSORPTION

CHARACTERISTICS OF THE PROCESS

In the technology of wastewater treatment, adsorption is used to remove dissolved organic substances that resist removal by biological methods. Adsorption is a process that removes substances from the solution and joins them to the surface of the solid body--the sorbent.

Factors that influence adsorption are temperature, pH, and size of the sorbent particles. This last parameter influences the rate of adsorption but not the total adsorptive capacity of the sorbent.

The fact that activated carbon, because of its porous structure, has a very large surface area per unit of mass has spurred its use as an adsorptive material. It can be used in both powdered and granulated form. However, in the wastewater treatment process (unit reactors) granular carbon is more often used on account of its regeneration possibilities. The adsorption process makes it possible to remove specific refractory compounds, such as certain dyes, detergents, and other organics, from textile wastewater.

AIM OF INVESTIGATIONS

The aim of the investigations of adsorption on activated carbon was to determine the effectiveness of pollutant removal from biologically treated and filtered wastewater from Andrychow, when properly chosen kinds of carbon and conditions of operation are applied. The correct designing of the adsorption process in Andrychow required examination of the following detailed questions:

1. Determination of the pollutant content and level of removal in wastewater subjected to adsorption, with particular attention to indicators characteristic of wastewater from the textile industry--that is, COD, color, and detergents;
2. Definition of a method of evaluating activated carbons that would allow for an accurate and quick determination of the suitability and economy of using a given carbon for removing refractory pollutants;
3. Choice of an activated carbon with the most favorable technological and economical indicators for the wastewater from Andrychow;
4. Determination of operational parameters of the adsorption process, such as the individual carbon load, the contact time, the wastewater flow rate through the bed, and the granulation of the carbon; and

Analysis of Standard Methods of Evaluating Carbon

The Polish Standards [40] give the following parameters characterizing the physicochemical properties of carbon: maximum moisture; maximum ash content; maximum content of substances dissolved in water and in hydrochloric acid; content of tar and oil substances; maximum content of ions Ca, Fe, Cu, S, SO_4, NO_3, C, CN and of heavy metals converted to Pb; pH value; and granulation. Moreover, for some carbons bulk density, mechanical endurance, abrasion number, water absorptivity, dynamic activity, and content of volatile solids are given.

The adsorptive capacities of different types of carbon are characterized with the help of the methylene and milligram numbers. The milligram number (MG) is the number of milligrams of the activated carbon under examination necessary to remove the color from 200 ml of a model solution of molasses. The purpose of this is to obtain a level of color removal comparable to that obtained with a standard carbon, where the standard carbon is a comparative carbon with a milligram number of 270 [40]. The model water solution of molasses should decolor to such a degree as to give 67 to 68 percent adsorption of light in the Lang Colorimeter or 32 to 33 percent permeability of light in the KF-3 colorimeter with a yellow filter. This corresponds to a decoloration property of carbon equal to 270 MG.

The methylene number (LM) is the number of milliliters of 0.15 percent water solution of hydrated methylene blue, decolored by 0.2 g of activated carbon [40].

The physicochemical parameters of the chosen carbons are given in table 8-1. The data on Polish activated carbons were obtained from the catalog [41] or directly from the producer, the Carbon Electrode Plant in Raciborz. Some missing data such as bulk density, pH, and granulation of the American carbons were determined individually in the IMWM laboratory on the basis of Polish Standards [40]. The methylene number for the American carbons was determined in the Carbon Electrode Plant laboratory.

Studies of the Porous Microstructure of Activated Carbons

Analyses of the porous microstructure of the carbons used--Calgon, Hydrodarco, Z-4 and ARZ--were carried out in the Physicochemical Research Center of the Main Mining Institute in Katowice.

Methods of Determining Porous Structure--

The capillary volume distribution with regard to measurements of radius in the range 75,000 Å and below 15 Å was determined by means of the porozimetric and porometric methods [42,43]. Moreover, the weight of each of the samples of activated carbon was determined using mercury as a pyknometric fluid [42]. Examination of porosity in the range of the pore radius 75,000 to 100 Å was carried out on a Carlo-Erba mercury porosimeter by forcing mercury into the carbon under pressure. However, capillary volumes with radii less than 100 Å were determined on the DHL-3 sorptive porometer by its granulated form (which is suitable in adsorptive columns), and its relatively low price, is widely used in Poland for the removal of pollutants from wastewater. Carbon ARZ has exceptionally good mechanical endurance and physicochemical parameters and is intended primarily for the adsorption of gases. On the basis of introductory tests, ARZ was applied to studies of the adsorption of pollutants from wastewater. Hydrodarco and Calgon, supplied by the EPA, are used in the U.S.A. for wastewater treatment.

SAMPLING AND SCOPE OF PHYSICOCHEMICAL ANALYSIS

Both biologically treated, filtered wastewater and biologically treated, coagulated, filtered wastewater were collected for study of the adsorption process.

Wastewater samples were collected for test investigations once every hour and were averaged every 24 h. For laboratory scale work, however, samples were collected twice each week, when the wastewater from the inflow and outflow after the adsorption columns was changed, in amounts sufficient for 2 to 3 d of investigations. Laboratory tests were conducted only with biologically treated and filtered wastewater. During the course of the adsorption process a number of physicochemical parameters, controlling or complementing the investigations, were determined. Laboratory investigations covered temperature, pH, color, anionic detergents, BOD_5, and COD.

Organic carbon was determined at random in the test investigations when the adsorption isotherm was being marked out. The range of analytical determinations in the pilot investigations, however, included temperature, pH, color, nonionic detergents, COD, and BOD_5. For biologically treated, filtered, and coagulated wastewater, total organic carbon and nonionic detergents were also determined.

PHYSICOCHEMICAL CHARACTERISTICS OF ACTIVATED CARBON

Introduction

Determining the right criteria for selection of a suitable carbon for treatment of wastewater from Andrychow presented many difficulties. Hitherto, methods to determine the adsorptive capacity of carbon have not been defined. The choice of appropriate methods was made more difficult, in particular, by the appearance in the wastewater of organic compounds with varied composition and insufficiently known structures.

A series of physicochemical methods is applied to characterize approximately the properties of carbon. On this basis, it is possible first of all to estimate the usefulness of a given kind of carbon for removing pollutants characteristic of the wastewater. The methods used in the work to define the properties of activated carbon are described below. Among these methods are the standard methods used by producers, the examination of carbon microstructure, and the FINAD index.

Analysis of Standard Methods of Evaluating Carbon

The Polish Standards [40] give the following parameters characterizing the physicochemical properties of carbon: maximum moisture; maximum ash content; maximum content of substances dissolved in water and in hydrochloric acid; content of tar and oil substances; maximum content of ions Ca, Fe, Cu, S, SO_4, NO_3, C, CN and of heavy metals converted to Pb; pH value; and granulation. Moreover, for some carbons bulk density, mechanical endurance, abrasion number, water absorptivity, dynamic activity, and content of volatile solids are given.

The adsorptive capacities of different types of carbon are characterized with the help of the methylene and milligram numbers. The milligram number (MG) is the number of milligrams of the activated carbon under examination necessary to remove the color from 200 ml of a model solution of molasses. The purpose of this is to obtain a level of color removal comparable to that obtained with a standard carbon, where the standard carbon is a comparative carbon with a milligram number of 270 [40]. The model water solution of molasses should decolor to such a degree as to give 67 to 68 percent adsorption of light in the Lang Colorimeter or 32 to 33 percent permeability of light in the KF-3 colorimeter with a yellow filter. This corresponds to a decoloration property of carbon equal to 270 MG.

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Discussion of Results of Investigations--

Calgon has a considerable total surface area, S = 866.9 m^2/g, and the lowest total capillary volume, $\Sigma\Delta V = 0.8339$ cm^3/g, of the granular carbons studied. Its largest capillary volume, $\Delta V = 0.3470$ cm^3/g, appears in the capillary radius range of < 15 Å. Hydrodarco shows a considerably lower grain porosity. It has a total surface area, S = 534.8 m^2/g, and the highest total capillary volume, $\Sigma\Delta V = 0.9612$ cm^3/g, of the carbons studied. Its largest capillary volume, $\Delta V = 0.4020$ cm^3/g, is in the radius range of 15 to 150 Å. Granular carbon Z-4 has a smaller total surface area, S = 432.6 m^2/g, than Calgon and Hydrodarco. At the same time, carbon Z-4 shows the highest total capillary volume, $\Sigma\Delta V = 1.3487$ cm^3/g, and displays its greatest capillary volume, $\Delta V = 0.4123$ cm^3/g, in the capillary radius range of 15,000 to 75,000 Å. The shaped, activated carbon ARZ exceeds the all-granular activated carbons under consideration in both total surface, S = 1,056.4 m^2/g, and porosity, $\Delta V = 0.4600$ cm^3/g, in the micropore range of < 15 Å, while its total capillary volume is $\Sigma\Delta V = 0.9524$ cm^3/g.

These microstructural investigations characterize porous materials only with respect to capillary volumes equivalent to their radii. From these investigations, it is not possible to draw any conclusions about the shape of the pores or their distribution in the carbon grain.

Investigation of Adsorptive Properties by the FINAD Index

Subject and Assumptions--

The FINAD index proposed by Gomella [44] is a five-figure number referring to the determination of five parameters: phenol (F), iodine (I), indole (N), phenazone (A), and detergents (D). The individual components of this number are defined as follows:

- The phenol number is the amount in grams of the carbon dried at 105° C, crumbled and sifted through an 0.08-mm sieve, necessary to decrease a concentration of 1 l of phenol C_6H_6O solution from 0.1 mg/l to 0.01 mg/l.
- The iodine number is the amount of iodine, in grams, adsorbed by 100 g of carbon, which has been dried at 105° C, crumbled and sifted through an 0.08-mm sieve.
- The indole number is the amount of carbon in grams dried at 105° C, crumbled and sifted through an 0.08-mm sieve, necessary to decrease the concentration of 1 l of indole C_8H_7N solution from 0.6 to 0.1 mg/l.
- The phenazone number is the number of grams of phenazone $C_{11}H_{12}ON_2$ adsorbed by 100 g of carbon, which has been dried at the temperature 105° C and crumbled and sifted through an 0.08-mm sieve.
- The detergent number is the amount in grams of carbon dried at 105° C, crumbled and sifted through an 0.08-mm sieve, necessary to

decrease the concentration of 1 l of sodium lauryl sulphate $C_{12}H_{25}OSO_3Na$ from 0.25 mg/l to 0.025 mg/l.

The FINAD tests were carried out on four kinds of fresh carbon: Carbopol Z-4, Calgon, Hydrodarco and ARZ. Spent carbon Z-4 was tested after being applied in the two-stage column adsorption process carried out in the third series at the pilot plant in Andrychow. The symbol AD_1 signifies carbon used in the first stage of adsorption, and AD_2 refers to carbon from the second stage. The investigations were carried out at room temperature using water solutions of adsorbed substances. After being dried, the tested carbon was sifted through a 0.075-mm sieve. Gomella's work [44] was used in determining the FINAD index. However, analytical procedures were developed individually or modified on the basis of the literature. These are specified in appendix B.

Discussion of Results--

Using the calculation method given in appendix B, an interpretation of the results of the determination of phenol, indole, and detergent numbers is presented in figures 8-1, 8-2, and 8-3. The iodine and phenazone numbers are calculated from the formulas. Number grades representing the amount of carbon are assigned in the table in appendix B. Grade 0 indicates very poor, while grade 9 indicates very good adsorptive capacity for the substances under consideration. The FINAD indexes are presented in column form in figure 8-4.

For all the activated carbons examined by the FINAD method, the detergent index was highest, indicating that the carbons under examination are equally effective in removal of anionic detergents. The FINAD classification indicates that the best carbon for removing pollutants in water and wastewater is Calgon, which has the most balanced FINAD index. The Polish carbon ARZ has similar properties. The other tested carbons, Carbopol Z-4 and Hydrodarco, have approximately equal adsorptive capacities, but according to the FINAD test, they ought to be less effective in removing pollutants from water and wastewater. Investigations of used carbon Z-4 with the symbols AD_1 and AD_2 showed, as expected, a considerable lowering of the adsorptive capacities of carbon in the two-stage adsorption process. At the same time, this indicates that the carbon exhausts more in the first column (AD_1).

Summary of Results and Evaluation of Methods of Characterizing Carbon Properties

The ways presented here for defining the properties of carbon describe its physicochemical parameters, which undoubtedly have significance in the adsorption process, and also its adsorptive properties with regard to the substances chosen. Since the adsorption process is complex, it is possible to state only generally that carbon that adsorbs certain defined substances well is effective in removing other substances, especially substances in a mixture of various compounds. It seems appropriate, however, to apply different methods to obtain a fuller characterization of carbon, although probably it is only investigations on particular sources of wastewater that can determine its usefulness.

It seems that both the FINAD index and the laboratory test recently proposed by Gomella [45], which is carried out in the column with a layer of granulated carbon on three standard organic compounds with different particle size (butyl acetate, indole, and acridine), reflect only to a certain extent the adsorptive properties of the given carbon. But they do allow for an approximate choice of the most suitable type of carbon for removing defined organic substances from water.

All the results obtained by various means suggest that Calgon has the best parameters: large total surface, very well developed microporous structure, high bulk density, and well balanced FINAD index. Carbon ARZ, which has been produced experimentally for the adsorption of gases, also proved effective as an adsorbent of substances from solution. Carbons Z-4 and Hydrodarco have similar parameters and adsorptive capacities, expressed by the methylene number and FINAD index. They are likely to be less effective than Calgon and ARZ in the removal of pollutants from wastewater.

The aim of all these investigations was to choose a carbon suitable for the removal of color, detergents, and other refractory substances from biologically treated wastewater from Andrychow. Further studies carried out directly on wastewater should reveal whether and to what degree the properties of the carbons described here are useful in treating particular wastewaters.

TECHNOLOGICAL LABORATORY INVESTIGATIONS

Objective and Scope of Investigations

The investigations involved a series of chosen tests on biologically treated and filtered wastewater. First of all, tests were performed in a batch system on suitably prepared granulated carbons. The aim of these investigations was initially to distinguish the capacity to remove color, COD, and detergents; to compare the effectiveness of individual carbons; and to determine their adsorptiveness and the required introductory dose of carbon. Next, investigations were carried out in a continuous system, using beds of granulated carbons. These investigations were intended to check the adsorptive capacities of the chosen carbons in relation to specific wastewater pollutants and to examine the process in a dynamic system that simulated in detail the process conditions in the pilot station.

The investigations covered the following detailed questions:

- The influence of contact time on the removal of COD, detergents, and color;
- The adsorption isotherms for COD and organic carbon, and the influence of the carbon dose on percentage removal of COD, detergents, and color;
- The effectiveness of wastewater treatment in a continuous adsorption system tested in laboratory investigations;
- The adsorptive capacity of carbon in the continuous column adsorption process; and
- Regeneration of spent carbon.

Test Investigations

Influence of Contact Time on Pollutant Removal--

Method--In the first series 50 mg of carbon Z-4 and Calgon, individually crumbled, dried at 105° C, and sifted through a 0.075-mm sieve, were added at room temperature to filtered wastewater. The wastewater was subjected to vigorous batch mixing for 0.25, 0.5, 1, 2, and 4 h; then the carbon was separated on a Buchner funnel, and COD, detergents, and color were determined in the filtrate. In the second series, 300 mg/l of Calgon were used and samples were collected after 0.5, 1, 2, 3, and 4 h.

Discussion of results--The results of investigations, presented in figure 8-5, show a general decrease in the concentration of individual parameters of COD, detergents, and color as contact time of wastewater with carbon increases. The investigations confirmed that the establishment of an adsorptive equilibrium depends on the kind of pollutants in the wastewater at the time, on their concentration, and on the amount of carbon added. At the beginning, that is, for about an hour of contact time, a relatively quick decrease in the concentration of individual parameters was observed. As time elapsed, this degree of adsorption lessened, as was the case especially with color (carbon dose 300 mg/l) and detergents (carbon dose 50 mg/l); or removal stopped completely, as was the case with detergents (dose 300 mg/l) and color (dose 50 mg/l), where after only 0.5 h the concentration of detergents fell to a value of 0.02 mg and after 0.25 h color was determined at 25 mg/l. In view of the variable conditions in which the adsorptive equilibrium is established, contact times of 0.5 h and 1 h were chosen for a determination of the adsorption isotherm and for investigations of the influence of the carbon dose on the percentage removal of COD, detergents, and color.

Determination of the Adsorption Isotherm and Examination of the Effect of Carbon Dose on Pollutant Removal--

Method--Samples of carbon Z-4, Calgon, and Hydrodarco were crumbled, sifted through a 0.075-mm sieve, and dried at 105° C. Suspended matter was removed from wastewater by filtration after biological treatment or after both biological treatment and coagulation. Activated carbon in an amount from 0.005 to 0.1 g/l and 0.1 to 1.100 g/l was added at room temperature. The wastewater was mixed with the carbon for the chosen period of time (0.5 and 1 h), the carbon was separated on the Buchner funnel and the color, detergents, COD, and total organic carbon (TOC) by the 915A Beckman apparatus.

Discussion of results--The adsorption isotherms were plotted on log-log paper. C was plotted against x/m where C is the final concentration, x is the amount of adsorbed substance, and m is the weight of carbon used in the test. In order to determine the amount of substance adsorbed per unit weight of carbon at equilibrium with the influent concentration C_0, a vertical line is drawn at the point C_0 and the isotherm is extrapolated to the intersection with this line. The value x/m versus C_0 represents the amount of substance adsorbed per unit weight of carbon when the carbon is in equilibrium with the influent concentration.

The results of the tests are given in figures 8-6, 8-7, 8-8, 8-9, 8-10, and 8-11. The experiments performed in the first stage with small doses of Z-4 and Calgon (5 to 100 mg/l) showed increases in the removal percentages of detergent, COD, and color in the wastewater in proportion to the increase of carbon dose. The tests showed that Calgon in the range of the doses applied has better adsorptive capacities than Z-4. Differences in adsorptive properties were particularly apparent when a contact time of 1 h was used. However, after 0.5 h this dependence was not so clearly shown.

One of the tests intended to examine the adsorptive capacities of Z-4 at low pollutant concentrations (22 mg/l of O_2 COD and 0.136 mg/l of detergents) showed that Z-4 is not very useful. Increasing the carbon doses to 30 mg/l caused a lowering of the COD and detergent concentrations. However, a further increase in the dose to 100 mg/l did not improve the results; removal remained at 21 percent for COD and 66 percent for detergents (figure 8-6). In the second stage of investigations (figure 8-8), a dose of 100 to 1,100 mg of Z-4, Calgon, and Hydrodarco was used. It was found that the percentage of detergent removal increases as the dose of Calgon increases. However, beginning with a dose of 400 mg/l, removal with Z-4 grows slightly, while with Hydrodarco it remains at the same level. Similar dependence is shown for color.

The measurement of adsorptive isotherms for COD as shown in figures 8-9, and 8-10 indicates the great absorptive capacity of carbon Z-4 in both experiments at an influent wastewater concentration of 52.0 and 61.0 mg of O_2/l (0.60 and 0.62 mg of COD/mg of carbon) while less adsorptive capacity is indicated for Hydrodarco (0.42 to 0.46 mg COD/mg carbon), and the least adsorptive capacity for Calgon (0.16 to 0.165 mg of COD/mg of carbon). A sharp fall in the isotherm was found for Z-4, a gentler fall for Hydrodarco, and the least fall for Calgon. The angle of inclination of the isotherms was sharpest for the higher influent concentrations of COD.

The sharp fall of isotherms for carbon Z-4 and Hydrodarco indicates that the good adsorptive properties at higher concentrations are sharply reduced at lower concentrations. This confirms the previously observed low usefulness of carbon Z-4 for removing low pollutant concentrations. However, Calgon improves its adsorptive qualities in proportion to decrease in concentration, and this should be the best in batch treatment. Carbon Z-4 and Hydrodarco should be more effective in adsorptive columns [46].

The isotherm determined experimentally for the total organic carbon (TOC) (figure 8-11) basically confirms the results mentioned here. With Calgon, the isotherm had a sharper course than for TOC. The amount of total organic carbon adsorbed per milligram of carbon was as follows:

for Z-4	0.24 mg TOC per carbon,
for Hydrodarco,	0.13 mg TOC per mg carbon, and
for Calgon,	0.09 mg TOC per mg carbon.

It should be mentioned that the second series of test investigations and determinations of adsorption isotherms was carried out on batches of carbon Z-4, provided by the producer, with a methylene number 31. Hence, the results here are considerably more successful than in the first series. As a result of the inconsistent character of carbon, a certain divergence in adsorptive properties and the accompanying differences in effectiveness of pollutant removal should be expected.

Laboratory Technological Investigations in a Continuous System

Research Method--

The investigations were carried out in a continuous system using the experimental apparatus shown in figure 8-12, which consists of three adsorptive columns working in parallel. The characteristics of the adsorbents used for the investigations and the technological conditions of the process operation are given in table 8-3.

The experimental apparatus was installed in the experimental hall located in the basement of the Institute of Meteorology and Water Management in Cracow. The temperature of the room was adjusted to approximate the mean external temperature (about 15° C in summer and about 5° C in winter). The studies were carried out from April 11, 1975, to April 24, 1976.

Wastewater for study was collected twice a week at the pilot plant in Andrychow after biological treatment and filtration, and emptied into the influent wastewater tank with a capacity sufficient for 3 to 4 days working. This period was divided into individual series. At the same time, wastewater that had been collected in the treated wastewater tanks from the previous series was removed after averaging and collection of samples for analysis. The columns were supplied with wastewater continuously pumped from the influent tank. The working of the column was interrupted regularly twice a week when the wastewater in the influent tank was being changed, and once every few weeks during rinsing of the columns. In addition, work was interrupted if complications occurred in the biological treatment process at the pilot-activated sludge tank or if laboratory experimental units failed. Samples for analysis were collected from the influent wastewater tank and from the treated wastewater tank. In addition, a series of random samples was taken eight times from different column levels to determine the effectiveness of adsorption at different depths of the bed. Alkalinity, pH, COD, BOD_5, color, and detergents were determined in the samples.

Discussion of Results--

Method of presenting results--Pollutant removal on continuous flow adsorptive beds over the course of 87 sequential series is presented in figures 8-13, 8-14, 8-15, and 8-16. The effectiveness of pollutant removal at different depths of the bed is presented in figures 8-17 through 8-20. The total pollutant loads removed on used activated carbons are given in table 8-3. The relation of adsorption rate to concentration in the influent is shown in figures 8-21 and 8-22. In interpreting and discussing the results, the relation of the degree of adsorption to the factors discussed here was taken into consideration.

Degree of pollutant removal in continuous adsorption--The adsorption process studied was evaluated for its effectiveness in producing an economically justified degree of removal of pollutants common in textile wastewater. A decrease in wastewater pollutants after adsorption to values admissible for first class purity surface waters according to the Polish Standards (see appendix C) was accepted as approximately the authoritative degree of treatment. For example, for COD the admissible value is 40 mg of O_2/l, since the receiver of wastewater from Andrychow, which is ranked in the first class, at critical periods of the year has low flows close to 0. The concentration of pollutants in treated wastewater should be close to the standards fixed for a first class receiver. The pollutant concentration in the outflow from the adsorptive columns is presented in figures 8-13 to 8-16. The great variability in concentration of pollutants, the values of which in many cases depend on the composition of wastewater flowing to the columns, should be emphasized. Because of this variability, it is appropriate to give, when describing the effectiveness of the process, values of both pollutant concentration in the effluent and percentage of pollutants removed. The effectiveness of the process is differentiated for the various pollutant indicators:

1. COD in influent wastewater during the initial 5 mo was low, on average about 40 mg/l. Removal in all the columns was high--65 to 75 percent (according to Culp [46]--with a contact time of 45 min. COD removal was 75 percent. COD in the effluent of the adsorptive columns was 12 to 17 mg/l, depending on the kind of carbon. In wastewater that had passed through all the columns, COD was considerably lower than expected (figure 8-13). In September the portion of industrial wastewater in the mixture supplied to the pilot plant was increased to 66 percent. As a result, wastewater COD rose until February 1976, fluctuating from 50 to 120 mg/l. The average was 75 mg/l. At the same time, COD removal in the column with Z-4 and Calgon began to gradually decrease. Only in the column with ARZ was removal still high (about 50 percent, keeping the COD in the effluent at or below 40 mg/l up to the end of December 1975). In the later period, removal decreased successively in all the columns. It should be emphasized that removal did not increase distinctly when high concentrations appeared in the influent.

2. BOD_5 of wastewater supplied to the adsorptive columns was low--on average 9 mg/l--for the whole period of research (figure 8-14). From the beginning removal differed in individual columns. The lowest removal, averaging 45 percent, was found in the Z-4 column. The highest removal, 65 percent, occurred in the ARZ column. The BOD_5 load removed by 1 g of carbon in this period was approximately equal for all the columns (for Z-4, 0.046 g/g, for Calgon, 0.036 g/g, and for ARZ, 0.033 g/g). This situation was maintained until December 1975. It should be stressed that the increase in the proportion of textile wastewater in September 1975 did not cause an increase in BOD_5 in the influent wastewater. This BOD_5 increase, which only appeared in December 1975, was caused by the lowered effectiveness of the biological treatment plant. At the same time, from December 1975, BOD removal in all the adsorptive columns began to diminish distinctly. In the final period it was close to zero.

3. Wastewater color appeared in very different intensities. For the first 4 mo, however, the color concentration in the wastewater supplied did not have a distinct influence on the wastewater at the effluent from the columns filled with Calgon and ARZ. The color in wastewater from these columns did not exceed 15 mg of Pt, regardless of its concentration in the influent. But the color concentration in wastewater flowing out of the columns with carbon Z-4 was directly proportional to the color in the wastewater supplied. This confirms the results of the test investigations given in figure 8-8, which show that color removal on Z-4, as opposed to Calgon, increases slightly when the loading for 1 g of carbon is decreased. For this reason, color removal was close to constant, amounting to 50 to 60 percent. As the carbon was used up, the influence of initial color concentration was increased. A specific color was found in the wastewater after passing through all the columns. E. W. Lang [47] stresses that certain types of dyes are more difficult to remove from wastewater than are organic compounds, and that carbon for the treatment of colored wastewater should be chosen with a view to its adsorptive capacities in relation to color. The studies of colored wastewater from Andrychow showed Z-4 to be unsuitable for removing color.

4. For the whole period of laboratory research, anionic detergents in the wastewater supplied appeared in very small quantities. Practically, their amount did not exceed 1 mg/l. Detergent removal was high--for 6 mo over 80 percent. In the final period it underwent a decrease to about 75 percent for ARZ and Calgon beds and 45 percent for the Z-4 bed. These results confirmed the observations from Kostrzewa [48], which stress the ease with which detergents, especially nonbiodegradable ones, are retained by activated carbon on account of the relatively large size of their particles.

Comparison of adsorptive capacity and rate of its exhaustion in Z-4, Calgon, and Hydrodarco--In the investigations described in the previous section, large differences were found in the effectiveness of individual activated carbons in removal of the pollutants studied. This observation was confirmed by the results presented in figures 8-13 to 8-16 and 8-17 to 8-20. Detergent removal was good only with Z-4 and Calgon.

In order to compare the amount and rate of contaminant adsorbed per gram of carbon, the adsorption rate coefficient (value) was applied according to the formula:

$$U = \frac{x}{m} \times t$$

where

U = adsorption rate, in g/g/h;

x = amount of adsorbed contaminant during series $(C_o - C_e)q$, in g;

m = amount of carbon in column, in g; and

t = time period, in h.

These calculated values were related to the concentration of contaminant in the influent, C_o. Figures 8-21 and 8-22 give the results calculated for the first 20 series. From a comparison of the relation of rate to concentration in the relation calculated in figures 8-21 and 8-22, it is clear that adsorption does not occur on Z-4 at small initial concentrations when removing either COD or color. Only for Z-4 at a value of 30 mg/l is adsorption completely distinct; its rate increases quickly with the further increase in pollutant content in the wastewater supplied. But on Calgon and ARZ, adsorption already occurs at a value of 10 mg/l, and the rate increase as the concentrations increase is small. For other indicators this dependence was not clearly found.

As the adsorptive capacity of the carbon was exhausted, differences in effects became clearer. It should be assumed that this resulted mainly from the different loading by pollutants per gram of carbon in individual columns. For this reason, it seemed unnecessary in this case to compare beds that had equal volumes and ensured equal contact times. Figures 8-17 to 8-20 clearly indicate the large differences in pollutant removal, even in the upper layers of individual beds, where the greatest differentiation of unit loading of carbon occurs. In the deeper layers a certain leveling of effects occurs. As the carbon is used up, the deeper layers contribute more to pollutant removal. But the most active zone did not clearly move downward for any of the pollutant indicators.

The least regularity of removal at different depths was observed for carbon Z-4, which tends to form lumps only partially subject to separation during rinsing. Probably backwashing exerts some influence on the uniform exhaustion of the whole bed and causes partial mixing. This can occur to the greatest degree with Z-4, which has the smallest specific gravity. In the final period of investigations the adsorptive capacity of the beds at full depth simultaneously approached 0. This was seen most clearly when color was removed on carbon Z-4 (figures 8-19 d, e, and f).

The total adsorptive capacity of individual types of carbon was determined by calculating the COD loads removed by 1 g of carbon (table 8-3). These values are for all carbons lower than the 0.78 g of O_2/g of carbon determined at the South Lake Tahoe station [49]. By comparing the loads in the columns removed by 1 g of carbon with the adsorptive capacity determined on the basis of isotherms, it was found that with Z-4 they are approximately equal, amounting to 0.48 g of O_2/g for the continuous process and 0.62 g of O_2/g on the basis of isotherms. Greater differences were noticed for Calgon, where the value of 0.326 g of O_2/g was determined in the continuous process, and 0.165 g of O_2/g on the basis of isotherms. The increase in the load removed on Calgon in the continuous process in relation to the test investigations can be explained by the influence of total contact time of contaminants with carbon. As shown in figure 8-5, COD removal on Calgon was about 50 percent after 4 h. The decrease in the adsorptive capacity of Z-4 in the continuous process can be explained by its exhaustion before the adsorption of other pollutants, not all of which were determined in the analyses. Z-4 is characterized by large pores (table 8-2), resulting in the adsorption of primarily large particles. In the case of biologically treated wastewater, these can be microparticles of activated sludge or organic compounds, which have not been adsorbed by the carbon with small pores. Moreover, the laminar structure of the carbon makes it difficult during washing to eliminate dirtying of the surface of the carbon particles. This limits the penetration of pollutants into the depth of the carbon and decreases its adsorptive rate.

Irrespective of the influence of the results described above, it can be stated that when COD removal from wastewater from Andrychow is required only to an effluent concentration of 30 to 40 mg/l, the best carbon is Z-4, which is capable of removing the biggest load with 1 g of carbon. But when more thorough COD removal is necessary (down to an effluent level of 20 mg/l), Z-4 cannot be used. For small concentrations, considerably better removal is insured by Calgon and ARZ.

The results of studies of color removal are similar. Z-4 only partially removes color; decreasing the carbon loading gives slightly improved removal. But Calgon and ARZ with a small loading give complete color removal (figures 8-13 to 8-16).

Anionic detergents were removed well by all three kinds of carbon. Since they appear in small quantities, they are easier to remove than other pollutants, and they do not limit either the loading of single carbon or the period of the bed effectiveness.

Laboratory Tests of Activated Carbon Regeneration

Introduction--

In order to decrease the costs of the process of adsorption on activated carbon, carbon is submitted to repeated generation. Thermal regeneration is most often applied. In this process the organic substances adsorbed on carbon are evaporated and decomposed at several hundred degrees centigrade. The carbon arising from the decomposition of the organic substances partially blocks access to the pores and decreases the adsorptive capacity of the initial carbon. In this case an oxidant, most often superheated steam, is added.

In Poland, carbon regeneration has not been used up to this time on a large scale. Laboratory investigations of regeneration were carried out at the factory where the carbon is produced, the Carbon Electrode Works at Raciborz. The aim of this research was: to ascertain the degree of regeneration of spent activated carbon Z-4 after the double-stage adsorption process at the experimental pilot plant in Andrychow (the symbol AD_1 signifies carbon from the first column and AD_2 carbon from the second), and of the carbons Z-4, ARZ, and Calgon used in laboratory investigations in a continuous system; to watch the changes occurring as a result of this process; and to partially evaluate the regenerated product. In order to make a comparative evaluation of the result of regeneration, fresh carbon was also submitted to investigation.

Research Method--

Regeneration and all the analytical determinations were carried out on samples that had been previously dried at a temperature of 110° C. To find the proper temperature and regeneration time and to ascertain whether it is necessary to use water vapor, preliminary thermal regeneration tests were carried out on samples of 2 g, using a temperature of 700° to 800° C and a time of 6 to 40 min. It was accepted that a sufficient measure of the regeneration of the samples would be the recovery of their capacity to decolor methylene blue. The regeneration process was carried out in a laboratory activation unit with portions of 0.5 dm^3 of carbon. The retort was fitted with a temperature control device and water vapor generator, which was dosed in quantities of 300 g/h. The steam was superheated to the temperature of the regeneration process and, after the regeneration time required had elapsed, the carbon was emptied out of the retort into airtight tin cans to cool off. Next, the carbon was weighed and analyzed according to a standard method [40,42,50].

Results and Discussion--

A description of the physicochemical properties of spent activated carbons and fresh carbon is given in table 8-4. The results of regeneration of Z-4, ARZ, and Calgon are presented in table 8-5, and results of the regeneration of carbon with symbols AD_1 and AD_2 are presented in table 8-6.

The results for regeneration of Z-4 after the two-stage adsorption process (AD_1 and AD_2) indicate that carbon undergoes optimal regeneration at 800° C in a period of 12 to 15 min with the addition of superheated steam in amounts of 300 g/0.5 dm^3 carbon per h. The application of longer regeneration times leads to a further activation, associated with the raising of the methylene number, the water adsorptivity, total surface area, and subgrain. But, on the other hand, longer regeneration times cause losses connected with the decreasing of resistance to abrasion and of mechanical endurance. The average recovery obtained for carbon after regeneration varied from 80.6 and 85.3 percent.

Further tests of regeneration carried out on Z-4, ARZ, and Calgon, showed that reduction of the temperature of the process to 700° C would require prolongation of the time to 30 min. For ARZ and Calgon it was not necessary to use steam in regeneration. Z-4 was regenerated with steam added in amounts of 300 g/0.5 dm^3/h, keeping the temperature and regeneration time the same as for the remaining carbons. A satisfactory recovery of the adsorptive capacity of the carbons under investigation was obtained (see table 8-5).

It should be mentioned that these regeneration parameters obtained in the laboratory activation unit can diverge from those which would be applied on a technical scale. It is important that the investigations discovered the possibility of regenerating spent activated carbons in the process of adsorbing pollutants from Andrychow wastewater.

PILOT INVESTIGATIONS ON BIOLOGICALLY TREATED AND FILTERED WASTEWATER

Method of Conducting Research

The experimental apparatus was installed in the pilot plant in Andrychow. The temperature of the experimental room in summer approximated the average temperature of the surroundings--about 15° C; in winter it was maintained between 5° and 10° C. The temperature of the wastewater fed to the adsorption process did not differ essentially from the temperature of the room. After biological treatment and filtration the wastewater was pumped from the influent wastewater tank (where it had been kept for 1 h) to the pilot plant shown in figure 8-23. The plant operated continuously for 23.5 h daily with a daily interval of 0.5 h for backwashing the filtration columns. It did not operate on holidays or in periods when the adsorption columns were being washed or the equipment maintained. Samples for analysis were collected once for an hour from the pipes after the influent wastewater tank and after each of the columns. Analyses were conducted from the daily composited samples. Descriptions of the bed and the column operation parameters, as well as of the results, are given in table 8-7.

Course of Investigations

On the basis of the analyses of biologically treated wastewater, it was recognized that the adsorption process should achieve at least 30 percent COD removal. The investigations were then begun with a series with short contact times on carbon. In the first two series, one-stage adsorption was carried out with a detention time of 12 min. In further series, multistage adsorption was carried out with longer contact time. In all, five series of investigations were carried out on a pilot scale with new carbon.

Series I and II--One-Stage Adsorption--

A diagram of the experimental apparatus is shown in figure 8-23a. Series I was carried out from February 12, 1974, to March 23, 1974. Series II was carried out from April 24, 1974, to May 25, 1974.

Series III--Double-Stage Adsorption--

The scheme of installation is shown in figure 8-23b. Adsorption was carried out in two columns in series. Pressure formed by a water level in the equalizing tank was used to overcome head losses. The research lasted from August 28, 1974, to January 24, 1975.

Series IV--Three-Stage Adsorption--

The installation in figure 8-23b was used for the investigations. Three columns worked in series. Flow took place under hydrostatic pressure produced by the equalizing tank. The investigations lasted from March 3, 1975, to May 7, 1975.

Series V--

The investigations were carried out in parallel on two rows characterized by different wastewater flow rates and different granulations. The parameters of the process for both rows are given in table 8-7 and the scheme of the process in figure 8-23c.

Discussion and Method of Presenting Results

The course of pollutant removal on individual beds is given in figures 8-24 to 8-31 and 8-33 to 8-35. The operation parameters of the adsorptive beds in individual series are given in table 8-7. The total pollutant loads removed and the average of individual removal values are given in table 8-8.

Degree of Pollutant Removal in the Adsorption Process With Continuous Wastewater Inflow

On the laboratory scale, on fresh carbon Z-4, the COD, color, and detergent removal was over 50 percent even in the first layer with a contact of 10 min. But on the pilot scale, hardly greater than 20 percent removal was obtained in the first and second series with 12 min of contact. After several days of operation of the bed, this removal decreased to below 10 percent. The basic cause of such poor effects was the use of Z-4 from a different supply than that used on the laboratory scale.

The indicators characterizing the quality of both batches of carbon are given in table 8-1. They show that the adsorptive capacity of carbon from the first supply is less than that shown in the producer catalog. It should be emphasized that when there is a large variation in the influent concentrations appearing both in 24 h and in longer periods of time, such a low removal is difficult to distinguish. Therefore, only the average removal effects have been given (table 8-8).

The relation of adsorption rate to concentration in the influent is shown in figure 8-32. The graph indicates that on the pilot scale the increase in rate as the concentration increases is lower for COD and higher for color than on the laboratory scale. The dispersion of results for both indicators is considerably greater.

To improve the effects in later series, the contact time was prolonged by adding additional carbon reactors. As the contact time was prolonged, the total degree of removal increased, but as a rule it was still lower than the effects obtained with corresponding parameters on the laboratory scale, with the exception of the fifth series. The removal of individual pollutant indicators on the pilot scale was as follows:

1. In single-stage adsorption 18 percent of COD was removed in the first series, and 12 percent in the second. The average COD concentration in the effluent was 60 and 52 mg/l, respectively. On the other hand, average influent concentration for the first series was 73 mg of O_2/l of COD, and for the second one 59 mg of O_2/l of COD (table 8-8). In the third series in double-stage adsorption with the same parameters, removal of 18.9 percent on average was obtained in the first stage and an additional 6.5 percent in the second. The average COD concentration in the effluent was 48 mg/l. In the fourth series, with three-stage adsorption, a total removal of 50 percent was obtained in the first

period and 39 percent in the second period, where there was a lower concentration of COD in the influent wastewater. The concentration in the effluent in both periods was 22 mg/l on the average. In the fifth series, removal was high in both the single-stage and the double-stage adsorption processes, reaching 73 percent and 68, percent respectively. This can be explained only by the fact that up to the last series the Z-4 used had the same adsorptive properties as the Z-4 used in the column investigations on the laboratory scale.

2. The BOD_5 concentration of the wastewater after biological treatment and filtration was on average 8 mg/l during the first and second adsorption series. There was 18 to 25 percent removal of BOD_5 in the adsorption process. Wastewater BOD_5 in the effluent was on average 6 mg/l, but the maximum concentration exceeded even 10 mg/l. Investigations in the third series confirmed the results from the previous series regarding percentage of BOD_5 removal on one stage (20 percent). After double-stage adsorption, the effluent was characterized by a BOD_5 concentration of 4 to 5 mg/l. Further research in the series also confirmed the low removal percentage--10 to 20 percent--for a contact time of 12 min. Prolonging the contact time by introducing the third stage of adsorption did not increase the removal above 30 percent. To sum up, the results obtained are considerably lower than those obtained at the Pomona plant (which treated municipal waste) [51], where, on the average, 85 percent was removed on carbon, and 3 mg/l remained in the effluent.

3. Color was removed very irregularly. During the first two series no stability was found for either percentage removal or intensity of color in the effluent--although the color of the wastewater supplied was low during this period and its spectrometric character approximated the natural color level of municipal wastewater. During the third series there was an increase in color in wastewater supplied to the columns. A high specific color was very often found, and on those days removal was very small in both stages. During this series distinct removal occurred only on the first days. In the later period the adsorptive capacity of the carbon in relation to dyes was decidedly reduced, so that only slight removal occurred. The results from the fourth series were similar. During this series, in the first column, removal occurred initially at 36 percent and later at 20 percent, and in the second stage the average removal from the whole series was only 9 to 11 percent. In the third stage, color removal hardly took place. But in the fifth series a color removal of over 60 percent was obtained in both rows.

4. Removal of anionic detergents was about 30 percent in the first stage. During the first two series the detergent concentration in the influent wastewater was on average 4 mg/l, and about 2.5 mg/l still remained in the effluent. In later series the amount of detergent in the influent was lower than 3 mg/l, and in the effluent it slightly exceeded 1 mg/l after a second stage of adsorption had been added. The third stage of adsorption yielded an increase in the amount of detergents removed by another 30 percent. During the fifth series the amount of detergents

in the influent was very low (0.35 mg/l), and the removal in one stage over 70 percent. The results of this series confirm the differences in the quality of the carbon used in this series and in the previous series.

It should be stressed that in all the series discussed, the removal of both detergents and COD was considerably lower than for the same contact time on a laboratory scale. The detergent concentration in the effluent during the first through fourth series was not lower than 0.3 mg/l, regardless of both the detergent concentration in the influent wastewater and the contact time. But during the fifth series, when carbon of a higher quality was used, the detergents were removed to a level below 0.1 mg/l.

Influence of Adsorption Parameters on Pollutant Removal

The influences of three conditions of operation were analyzed in the investigations: contact time, carbon granulation, and flow rate through the carbon bed.

In choosing the operating conditions of the adsorptive bed, greatest attention was devoted to the influence of the time of wastewater contact with the activated carbon. The times most often recommended by the literature are 20 to 40 min [49,51,52]. In the present research, times of 12, 24, and 36 min were used, with constant surface loadings and the same carbon Z-4. The contact time was prolonged by adding successive stages of adsorption, and the ratio of carbon quantity to the flow was proportionally increased. The results, set out in table 8-8, indicate that the influence of contact time on removal differs for individual indicators.

The clearest dependence was found in the case of COD, where removal at each stage is slightly less than removal at the preceding stage. On Z-4 from the first supply, removal at one stage with a contact time of 12 min was 13 to 19 percent, and removal at three stages with a total retention time of 36 min was 39 to 49 percent. In the fifth series when Z-4 from supply II was used, a higher COD removal (67 to 73 percent for two stages), still proportional to the contact time, was obtained. Removal of BOD_5 clearly decreased at successive stages. High removal, about 20 percent, was found in the first stage; in the second and third stages together, during the 24-min contact period, removal was about 12 percent. The relation between removal and contact time for detergents was similar to that for BOD_5, but considerably higher effects, in percentages, were obtained. In the case of color, prolonging contact time did not clearly influence the effects. Significant removal occurred only in the first stage; in the second, removal was very small; and in the third, practically no removal took place. Likewise, no color removal in the second stage was found in the case of carbon from supply II. This was probably caused by the presence in the wastewater of color compounds that were not removable or were removable only partially in the process of adsorption on activated carbon Z-4.

The influence of carbon granulation on removal effects was examined in the fifth series. Z-4 of 0.75-mm to 1.0-mm granulation was used for the investigations. For all the indicators, better removal was found with a finer granulation.

E. W. Lang [47] quotes the results obtained by three authors, who, for the dependence of removal on the diameter of carbon grains, accept the equation:

$$E = \frac{1}{d^{a}}$$

where

E is the removal effect,

d is the diameter of carbon grains, and

a is the exponent given by various authors within the limits 0.5 to 2.9.

The investigations on wastewater from Andrychow found that the value of this exponent for individual pollutant indicators in the fifth series runs as follows: for COD, 0.31; for BOD_5, 0.37; for detergents, 0.32; and for color, 0.30.

The flow rate through the bed has no influence on treatment effects if it falls within the limits of 5 to 40 m^3/m^2h. Obtaining this rate in a full scale process does not usually present any difficulties, but in small scale investigations the use of beds several meters in height, required to achieve a longer contact time, is sometimes troublesome. For this reason, investigations were carried out in the fifth series to compare the effects obtained at 5.1 m^3/m^2h. Process parameters other than granulation were the same. Decreasing the rate was not found to have any influence.

Activated Carbon Requirements

In the wastewater from Andrychow, the adsorptive capacity of carbon was exhausted most quickly in relation to COD and color. Because of the great variability of color removal, COD removal should be accepted as the most suitable indicator for determining carbon requirements.

The first three series conducted in Andrychow showed that the adsorptive capacity of Z-4 is 0.13 g COD O_2/g of carbon to 0.27 g COD O_2/g of carbon. It should be emphasized that this carbon was of poorer quality than normal (table 8-1). In the laboratory investigations carried out in a continuous system, this value was 0.48 g COD O_2/g of carbon. Interpolating from the values inserted in tables 8-3 and 8-8, it can be accepted that for Z-4 conforming to the qualitative standard, the COD load removed by 1 g of carbon amounts to about 0.35 g/g.

The carbon demand for treating combined wastewater from Andrychow was calculated from the formula [47]:

$$M = \frac{C_o - D}{X_o} = \frac{75-40}{0.35} = 100 \text{ g/m}^3$$

where

M is the carbon demand expressed in grams to treat 1 m^3 of wastewater,

C_o is the average concentration of wastewater supplied to adsorption taken as 75 g of COD/m^3,

D is the admissible concentration of wastewater after adsorption. (as determined by the effluent concentration, taken as 40 g of COD/m^3), and

X_o is the adsorptive capacity required of the carbon used. (For standard Z-4, X_o was taken as 0.35 g/g. In relation to the value 0.479 determined in laboratory investigations, a factor of 75 percent was applied for design.)

Using 0.75, the Calgon and ARZ demand was calculated in the same way for a comparison on the basis of continuous laboratory investigations. This demand--160 g/m^3--is equal for both carbons. The second indicator in relation to which the adsorptive capacity of activated carbon is quickly exhausted is color. Calculation of carbon consumption as regards this indicator is, however, impossible on account of the great irregularity in its removal and the complete lack of stability in color intensity in the effluent. This makes it impossible to define the operating parameters of adsorptive beds, so that the dye removal effects are satisfactory. Exhaustion of the adsorptive capacity of carbon in relation to BOD_5 and anionic detergents occurs considerably later than in relation to color and COD. Because of the small concentration of detergents in the influent, the amount of detergents removed is too small to be easily determined analytically.

PILOT INVESTIGATIONS ON BIOLOGICALLY TREATED, COAGULATED, AND FILTERED WASTEWATER

Experimental Plant

The investigations were carried out at the pilot plant in Andrychow using the installation shown schematically in figure 5-13. After biological treatment, contact coagulation, and filtration on an anthracite-sand bed, the wastewater was directed to a tank from which it flowed by gravity to the adsorption columns. During the first series three columns were linked in parallel; during the second only one column operated; and during the third two columns linked in series operated. Calgon, Hdyrodarco, and Z-4 were used in these investigations.

Course of Investigations

Three series of investigations were carried out. Two of them were conducted on wastewater coagulated using the optimum coagulant dose (see section 7) for removing color and detergents (250 mg of alum). The last series involved wastewater coagulated with the optimum dose for removing nonsettlable suspended solids and colloidal solids (100 mg of alum and 1 mg of nonanionic polyelectrolite).

Series I--
The adsorption process was conducted in parallel, using three different kinds of carbon in order to compare the effects obtained with an equal loading of 1 g of carbon. The parameters are given in table 8-9. The research lasted from August 20, 1976, to October 9, 1976.

Series II--
The adsorption process was conducted on the third column filled with the Z-4 used in investigations in the previous series. The loading adopted was three times higher than that in the first series in order to determine the influence of loading on adsorption effectiveness. Conditions of operation are given in table 8-9. The research lasted from October 11, 1976, to October 16, 1976.

Series III--
The aim of the investigations was to ascertain the influence of the scope of previous coagulation on the degree of pollutant removal in the adsorption process. Two stage adsorption was carried out using Z-4. Parameters are shown in table 8-9. The research lasted from February 28, 1977, to March 26, 1977.

Discussion of Results

The course of removal is given in figures 8-36 and 8-37, and the average effectiveness in table 8-10.

In the first two series, biologically treated and coagulated wastewater was characterized by small concentrations of pollutants for all indicators. At the same time a very high level of removal was found in the adsorption process. COD and color in all columns were removed to a degree exceeding 80 percent. Concentrations in the effluent were many times lower than those found in adsorption of wastewater that had previously been only biologically treated. Removal of organic carbon (TOC) was also high, on average 65 percent, and the concentration in the effluent was on average 6 mg/l. The lowest percentage removal was found in the case of BOD_5, but the concentration in the effluent was only about 2 mg/l. When loading was increased threefold in the second series, some decrease in removal of BOD_5 and TOC was found. The pollutant concentrations in the effluent remained at the same level.

In the third series, coagulated wastewater was close in composition to the biologically treated wastewater given in table 8-8. COD removal by adsorption in this case was about 70 percent higher than in investigations using the same process parameters on noncoagulated wastewater (table 8-8, third series), but it was only 50 percent of the removal from wastewater treated with a large dose of coagulant (table 8-10, first and second series).

CONCLUSIONS

1. The effectiveness of treatment by adsorption of biologically treated mixed textile and municipal wastewaters depends on the correct choice of both carbon and process parameters, which should take into consideration the great variability in the composition of treated wastewater.

2. Because the correct choice of carbon is so important, it is necessary to take into account carbon characteristics such as bulk density, microstructure, adsorption surface, and methylene and milligram numbers. Where there are large organic pollutant concentrations in the influent, and where required concentrations in the effluent are not low, a carbon with a large pore volume should be chosen. But where a thorough treatment of low concentration wastewater is necessary, a carbon with a large adsorptive surface and small pores should be chosen. It was found that COD, BOD_5, and anionic detergents are removed on all carbons to a degree dependent on the process parameters, but color is fully removed only on carbons with large adsorptive surfaces.

3. On account of the conditions under which Andrychow combined wastewater is discharged, it was determined that, for biologically treated and filtered wastewater, the most appropriate adsorption occurs with Z-4 granulated carbon with 24-min contact time in relation to the empty bed. This allows for a degree of wastewater treatment that guarantees that the following effluent concentrations are not exceeded:

   COD--40 mg/l
   BOD_5--10 mg/l
   anionic detergents--2 mg/l.

   The average removal of the more important pollutants in all the investigation series was within the following range:

   COD--20 to 50 percent
   BOD_5--20 to 30 percent
   color--30 to 50 percent.

   Allowance should be made for the appearance of a specific color at certain periods as a result of only partial removal of some dyes.

4. Adsorption on activated carbon applied to wastewater after biological treatment and coagulation with a large dose of coagulant insures removal of specific pollutants that is about two times greater than the same adsorption used for biologically treated noncoagulated wastewater.

5. Allowance should be made for considerable qualitative differences within each kind of carbon, and carbon of each new supply should be compared with the accepted standard for the given kind.

6. By working out isotherms for the accepted carbon on the basis of test investigations of COD, organic carbon, or other pollutants contained in the wastewater under treatment, it is possible to assess the suitability of the carbon removing these pollutants. The maximum quantity of pollutants that can be adsorbed by 1 g of carbon determined on the basis of isotherms is applicable only when powdered carbon is used. With a granulated carbon, the maximum quantity should be considered an indicator for relative evaluation of different carbons.

7. Although it is time-consuming, the FINAD test is recommended in the case of wastewater or water with low pollutant differentiation and low concentration.

8. It was found that color is the most difficult pollutant to remove from Andrychow wastewater. Thus, obtaining the required degree of color removal is the most important factor when choosing a kind of activated carbon. But the COD load retained is the most meaningful for assessing carbon consumption, since the adsorptive capacity in relation to this indicator is exhausted most quickly. On this basis, and assuming an admissible COD of 40 mg/l after adsorption, it was found that the consumption of Z-4 which removes 0.6 g of COD/g of carbon will amount to 100 mg/l of biologically treated wastewater. With the same assumptions, this value will be 160 g/m^3 for Calgon and ARZ.

9. When different carbons are compared, the most important indicator is the weight efficiency of the carbon. Loading, both by hydraulic means and with a pollutant load, should be related to the weight and not the volumetric quantity of the carbon. When one kind of carbon with a constant bulk density is used, the volumetric loading of the carbon is comparable. The volumetric loading is inversely proportional to the contact time.

10. Carbon granulation has some significance when granulated carbon is used. Smaller carbon granulation allows the treatment effects to be increased while maintaining the same contact time. No influence of flow rate through the bed was observed.

11. Periodic washing of the adsorptive beds performed every 15 to 30 d increases pollutant removal by several percent. This is because of the elimination of the layer of suspended solids, which makes contact of carbon with the pollutants difficult.

12. The organisms developing on the bed were not observed to have any effect on pollutant removal. The concentration of oxygen did not undergo a distinct decrease in the course of the flow through the columns and varied from 2 to 4 mg/l. This oxygen excludes anaerobic processes, but aerobic oxidation can occur within a slight range. The negative influence of the growth of organisms on the clogging of the

filtration bed was slight, but frequency of backwashing was never shorter than 15 d.

13. An increase in removal efficiency of refractory substances was found on the carbon column after it had been out of action for several days. This phenomenon can be explained by the passing of pollutants more deeply into the carbon pores. Because of this, impregnation of the surface layer of carbon grains lessened, thus increasing the adsorptive capacity of the carbon in relation to newly supplied pollutants.

14. Laboratory investigations showed thermal regeneration of activated carbon at 700° to 800° C.

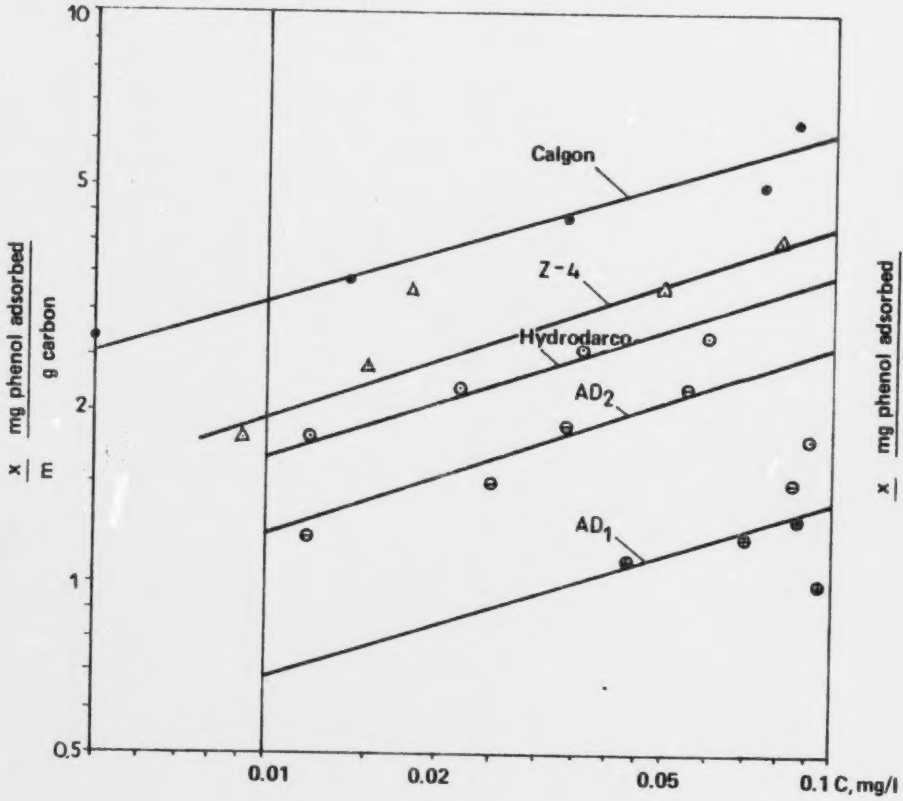

Figure 8-1. Determination of phenol number by the FINAD method.

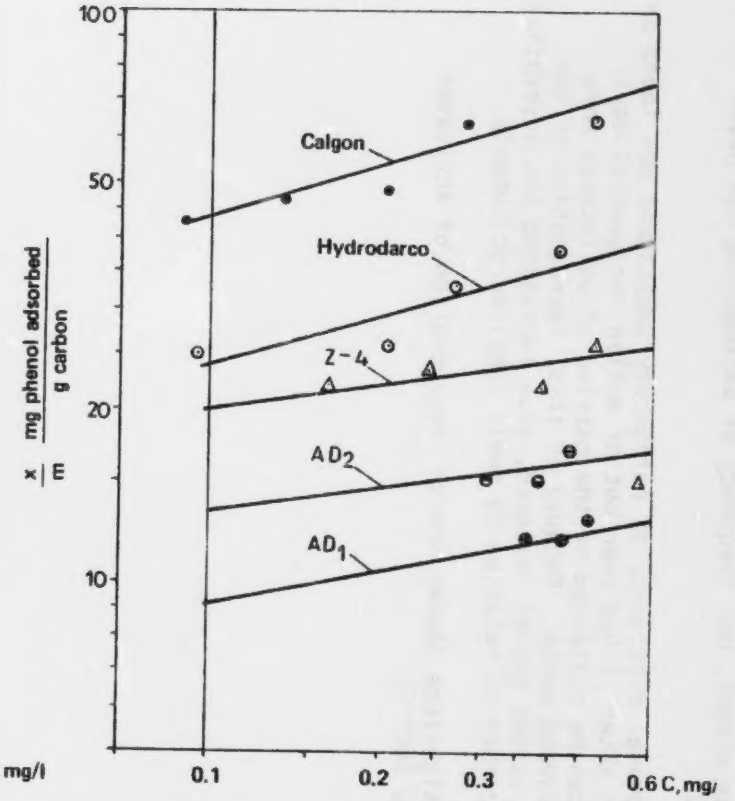

Figure 8-2. Determination of indole number by the FINAD method.

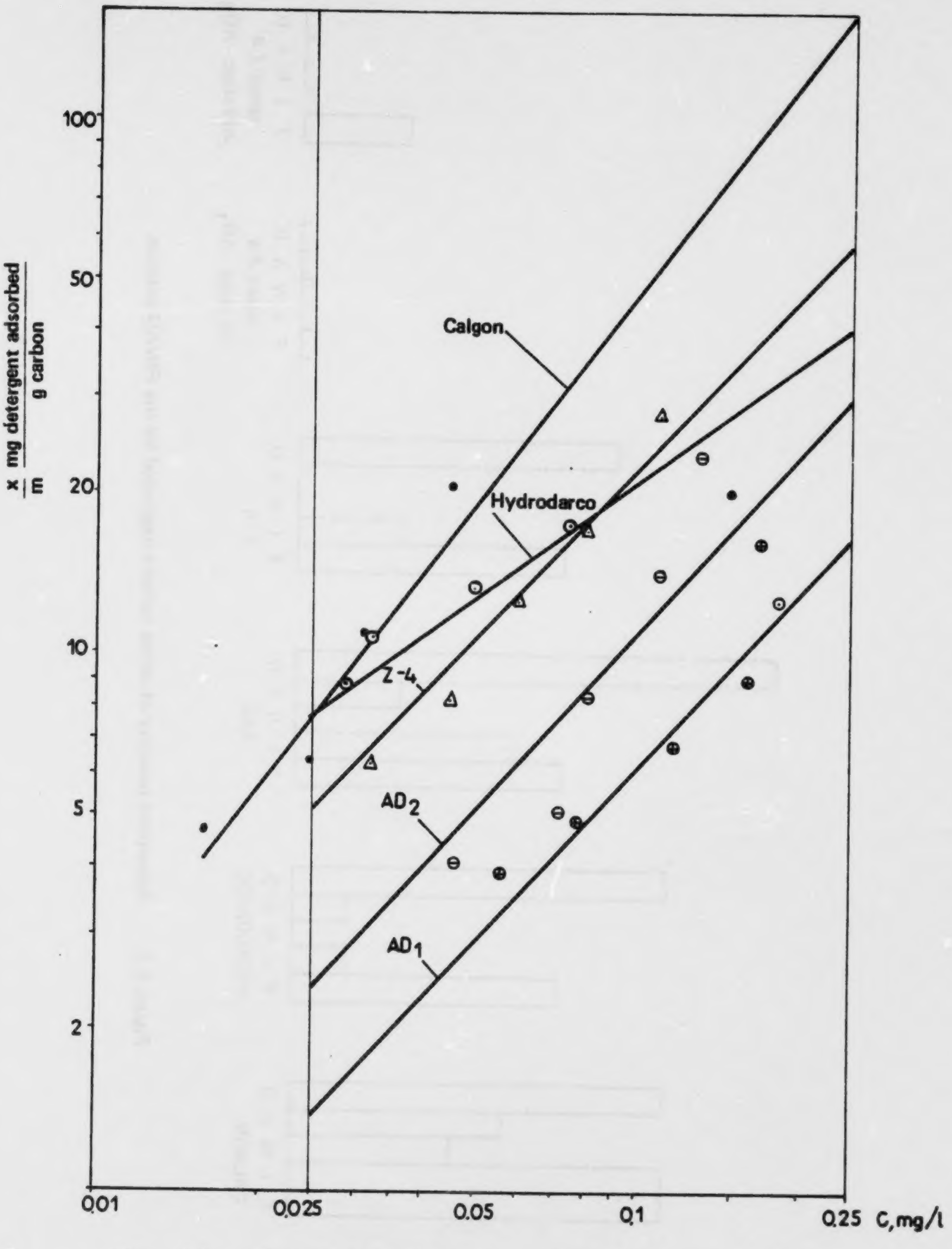

Figure 8-3. Determination of detergent number by the FINAD method.

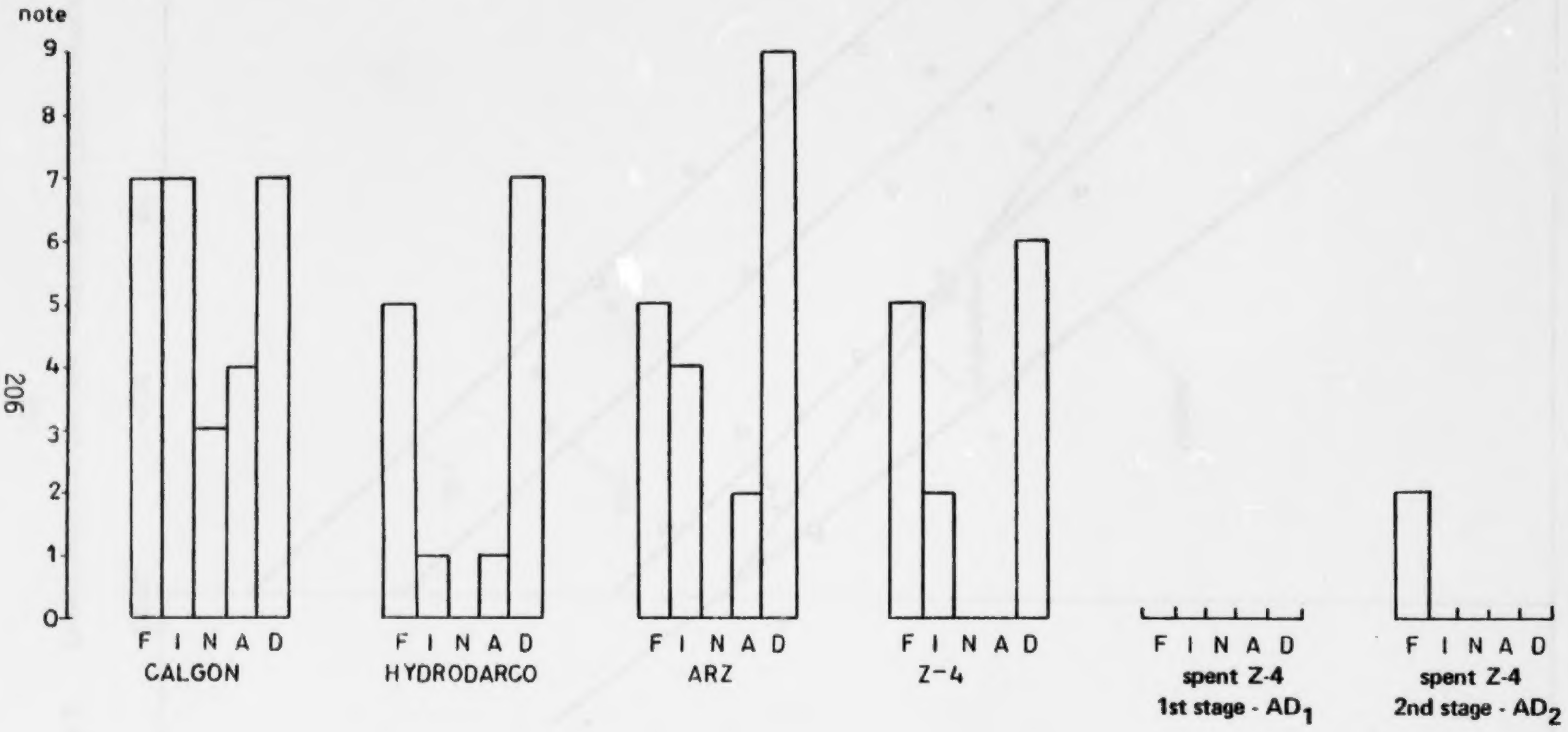

Figure 8-4. Adsorptive capacity of active carbons expressed by the FINAD indexes.

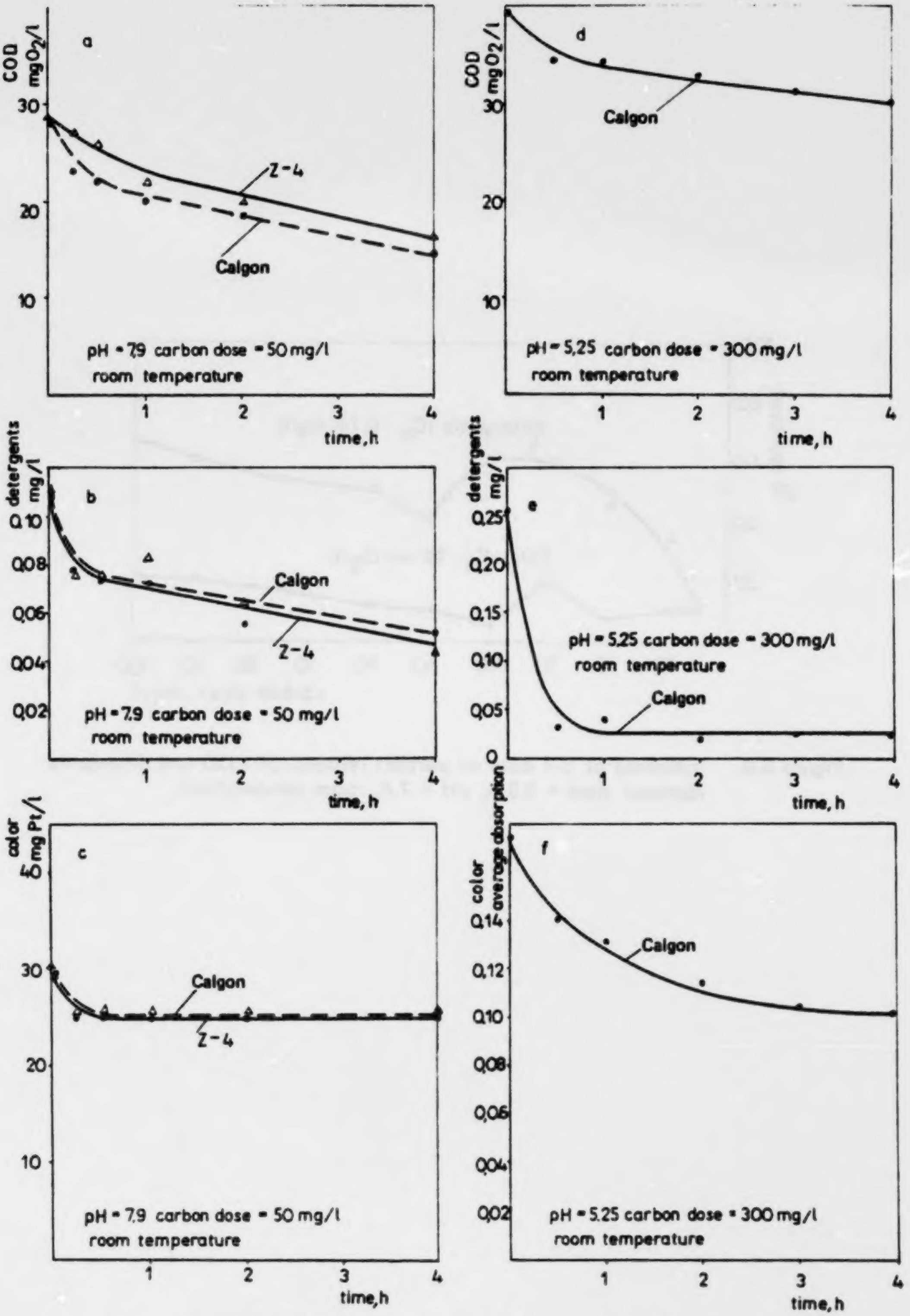

Figure 8-5. Influence of contact time on change of COD, detergent, and color concentration in wastewater treated with Z-4 and calgon.

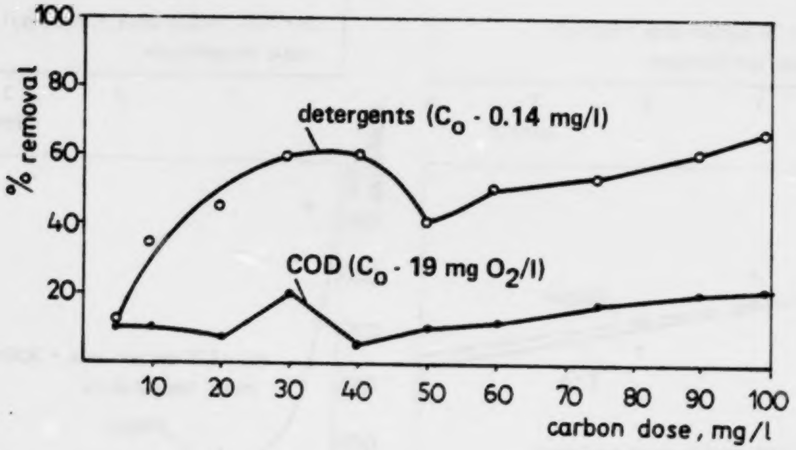

Figure 8-6. Influence of Z-4 dose on percent removal of COD and detergents (contact time = 0.5 h, pH = 7.8, room temperature).

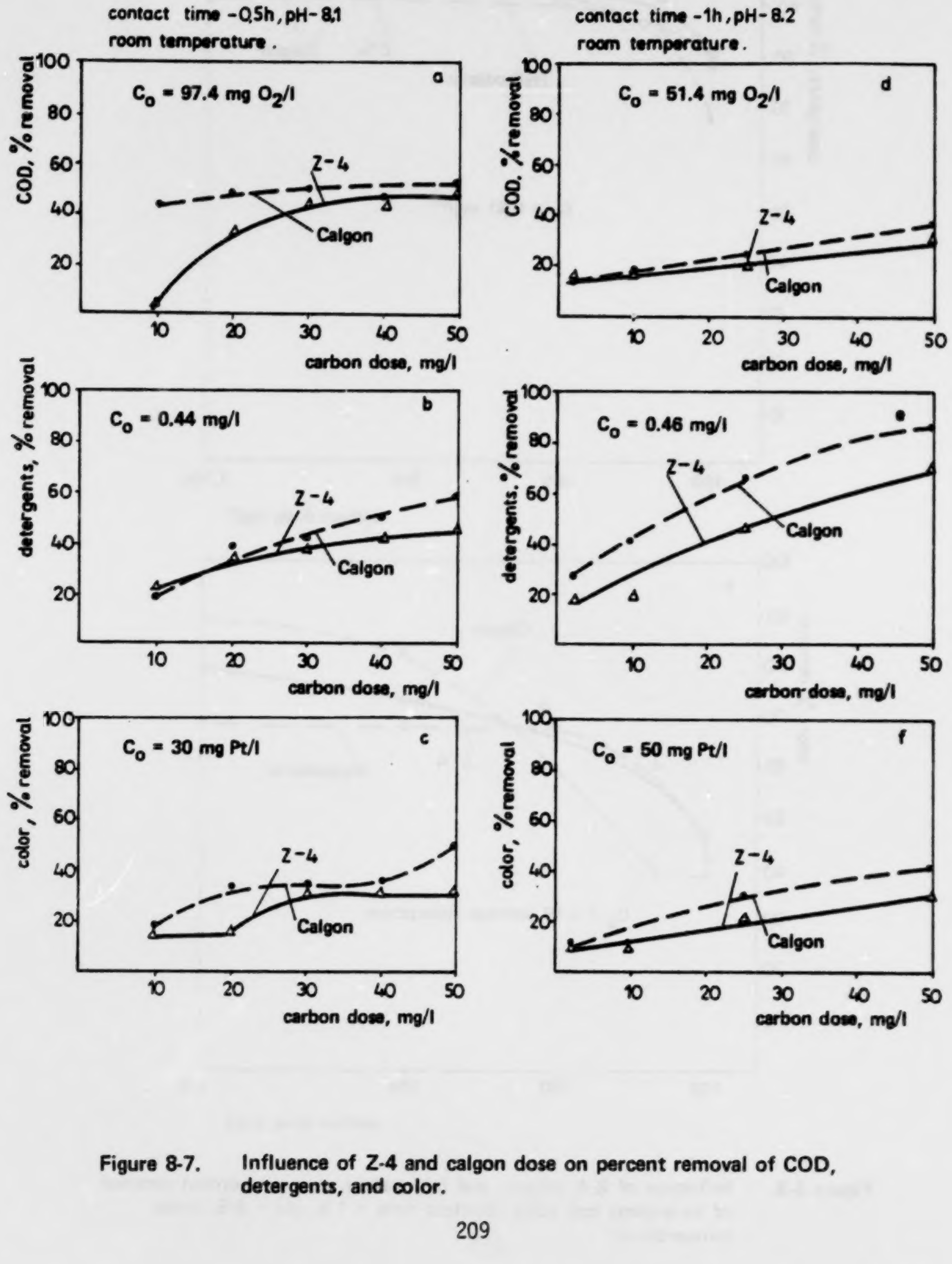

Figure 8-7. Influence of Z-4 and calgon dose on percent removal of COD, detergents, and color.

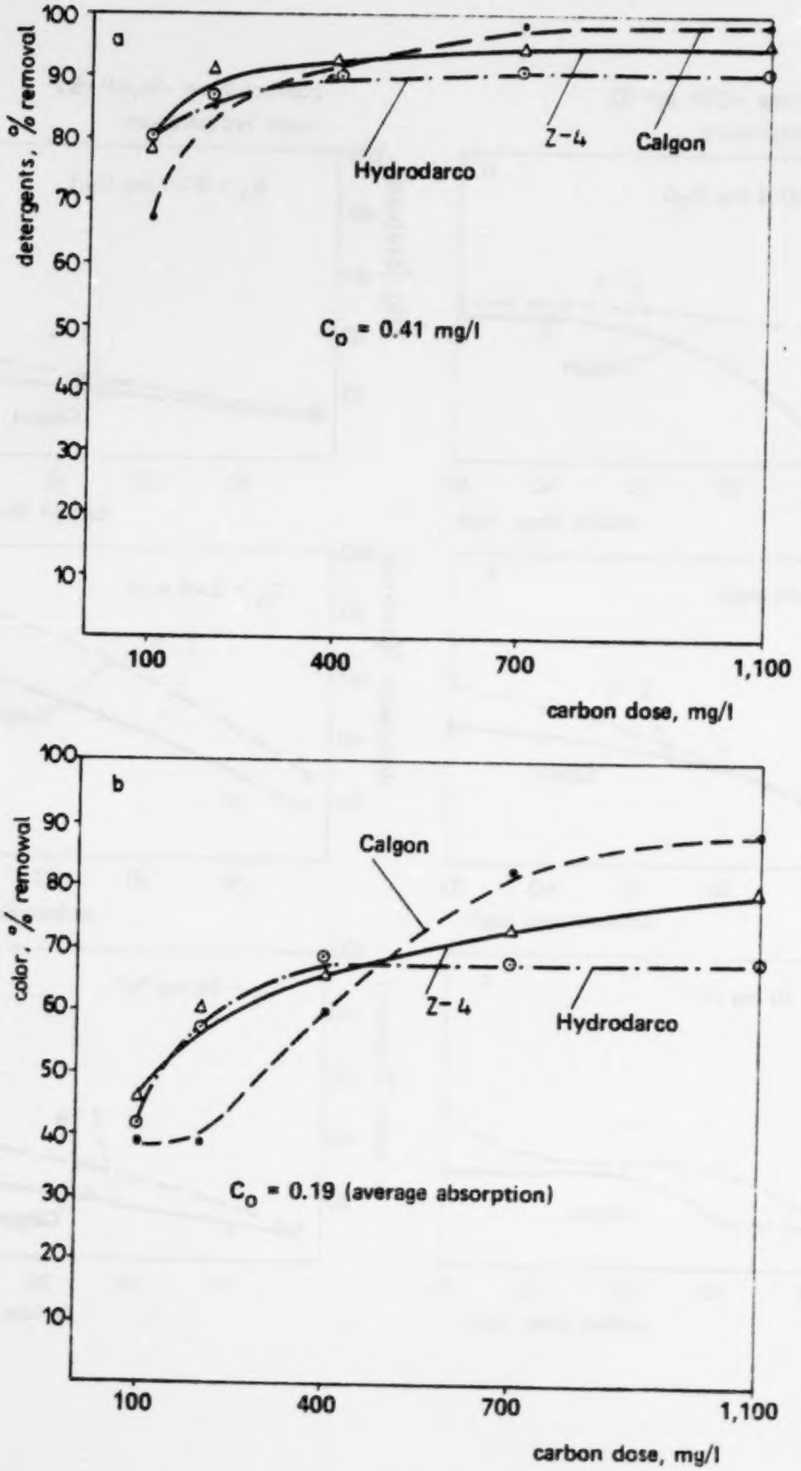

Figure 8-8. Influence of Z-4, calgon, and hydrodarco dose on percent removal of detergents and color (contact time = 1 h, pH = 8.5, room temperature).

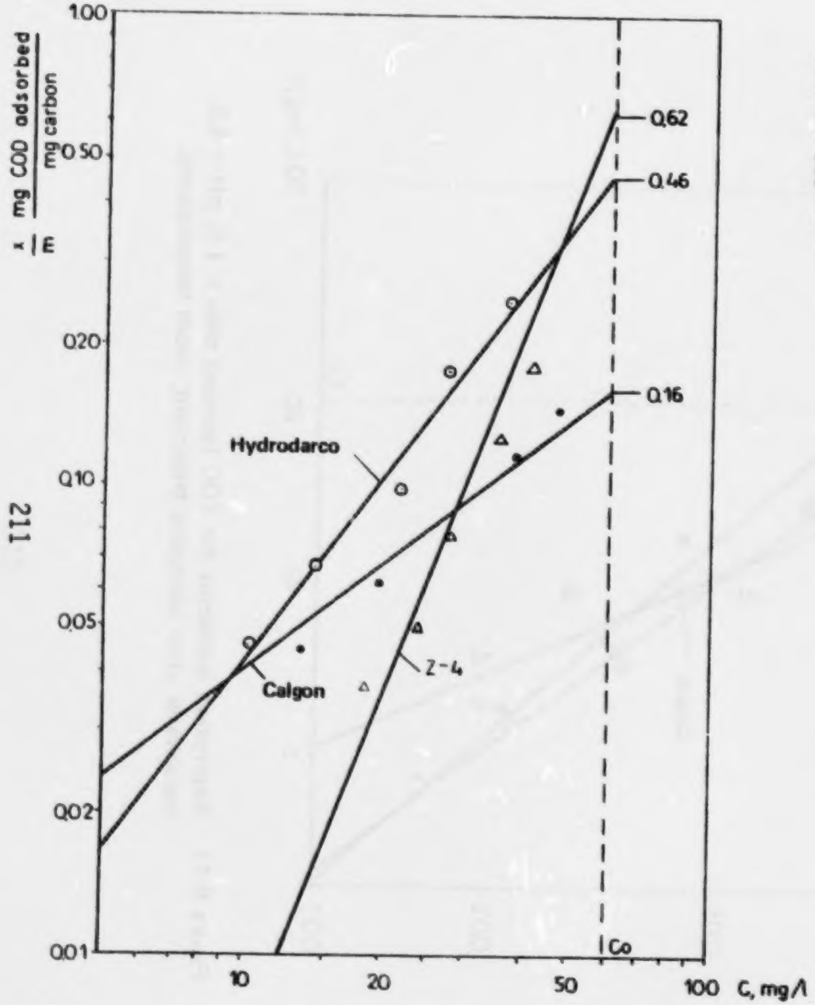

Figure 8-9. Adsorption isotherms for COD (contact time = 1 h, pH = 8.5, wastewater after biological treatment, room temperature).

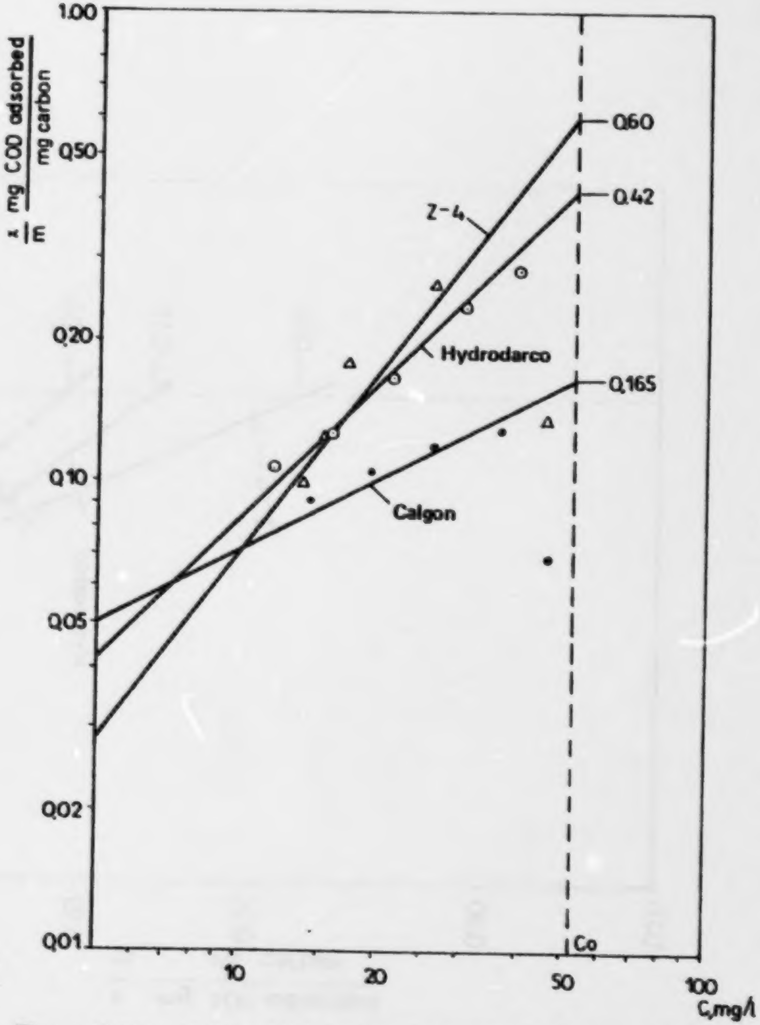

Figure 8-10. Adsorption isotherms for COD (contact time = 1 h, pH = 7.7, coagulated wastewater, room temperature).

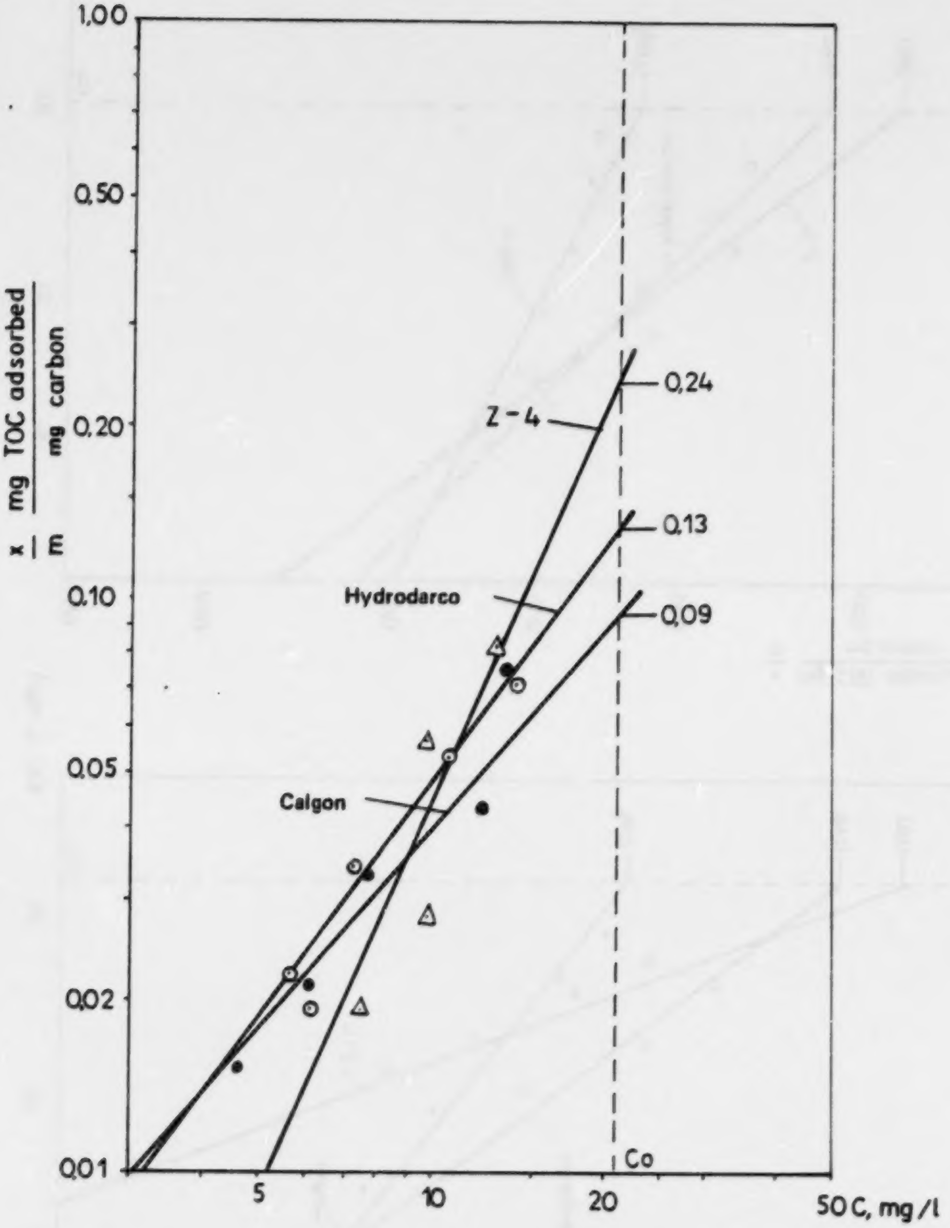

Figure 8-11. Adsorption isotherms for TOC (contact time = 1 h, pH = 8.5, wastewater after biological treatment, room temperature).

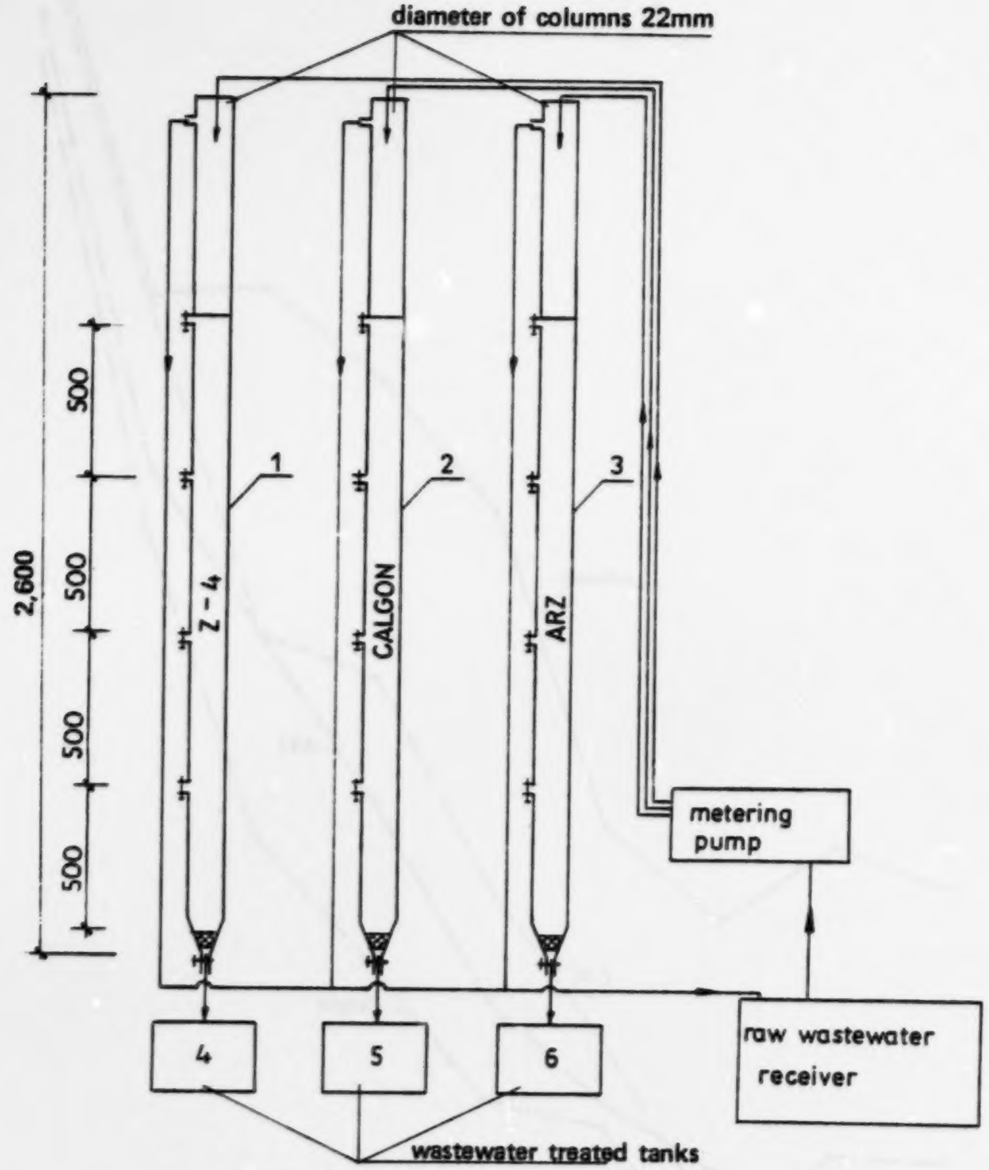
diameter of columns 22mm
2,600
500
500
500
500
1
2
3
Z - 4
CALGON
ARZ
metering pump
raw wastewater receiver
4
5
6
wastewater treated tanks

Figure 8-12. Scheme of a laboratory installation model for adsorption on activated carbon beds.

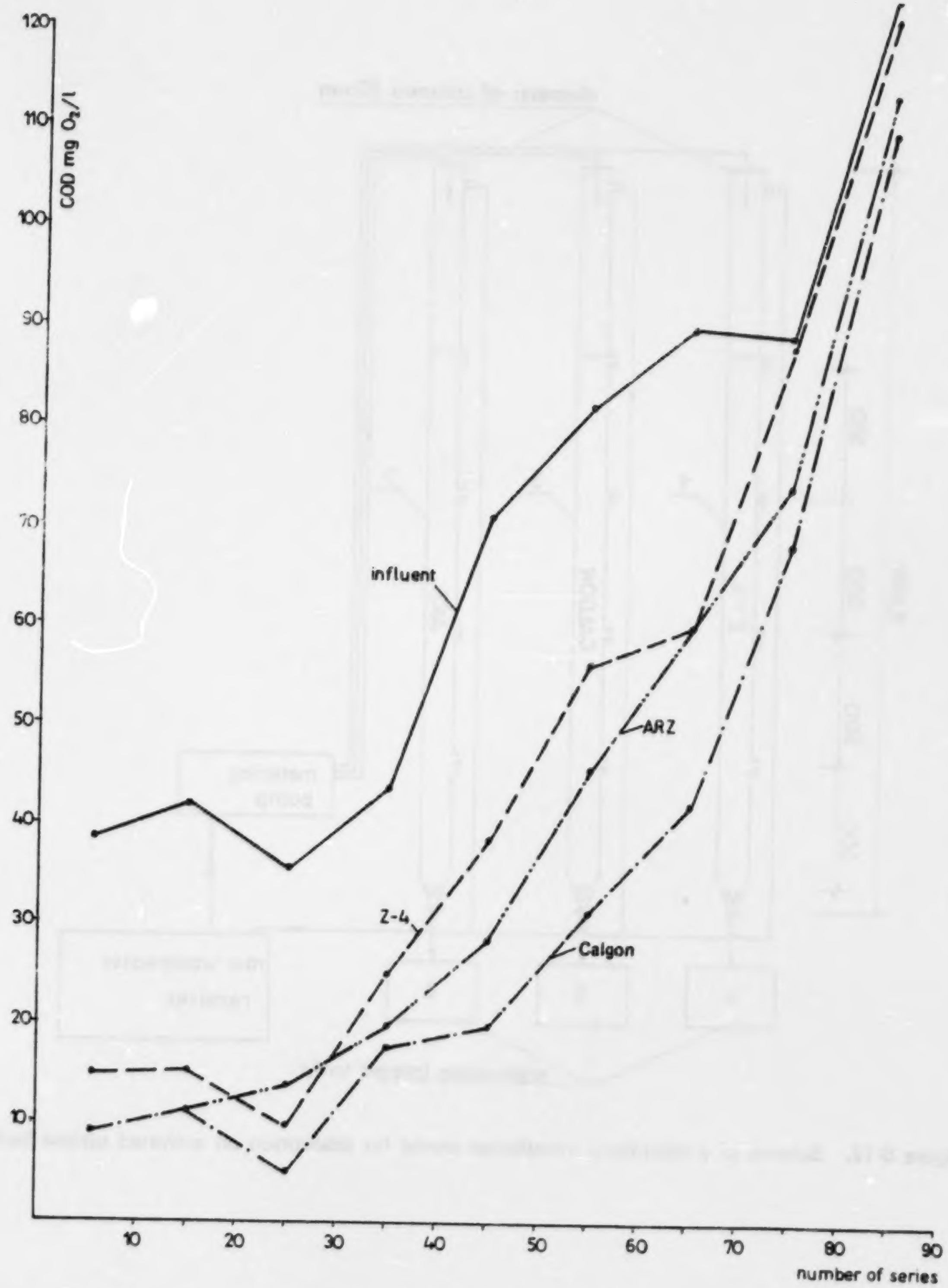

Figure 8-13. Course of COD removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale.

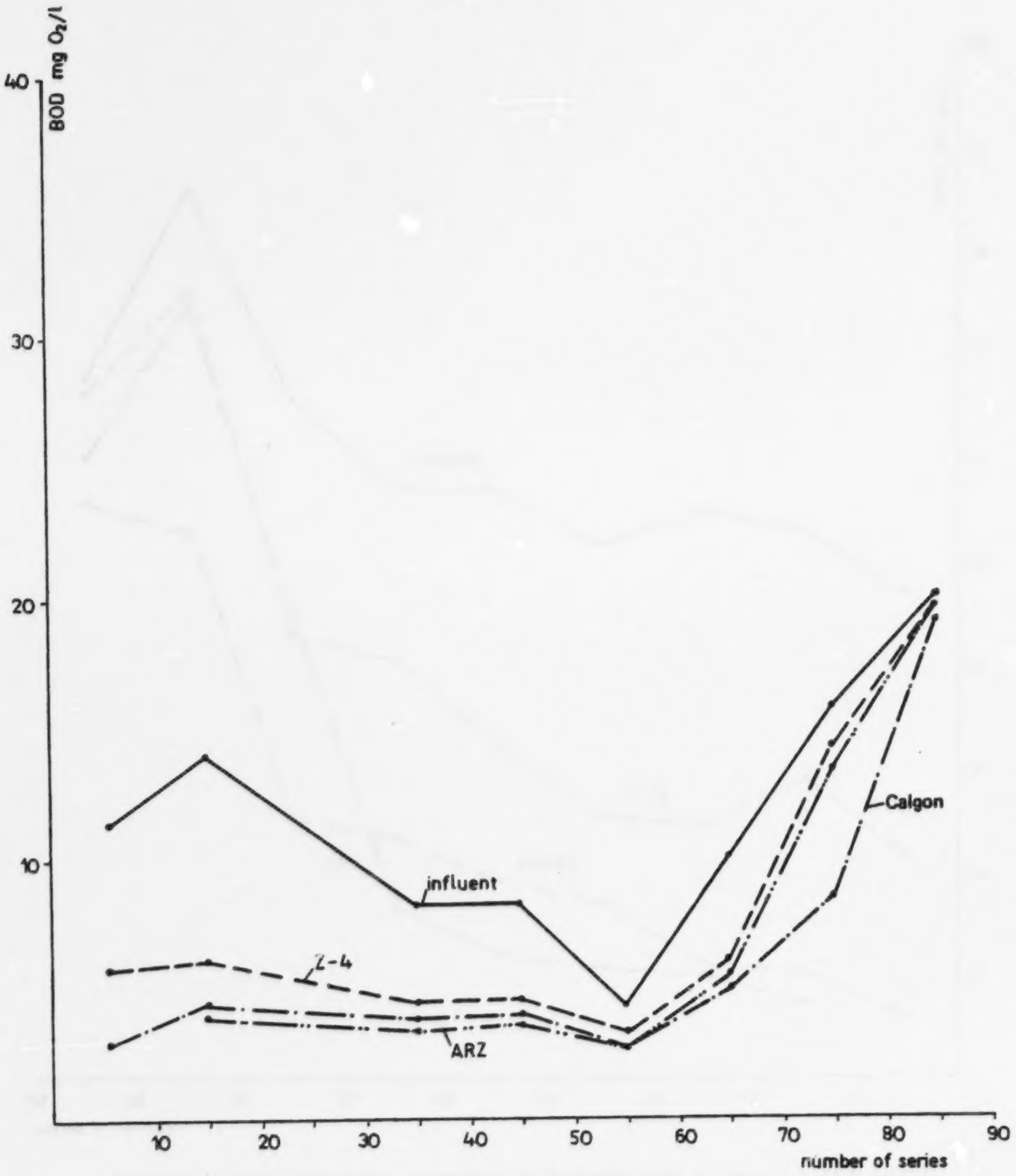

Figure 8-14. Course of BOD removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale.

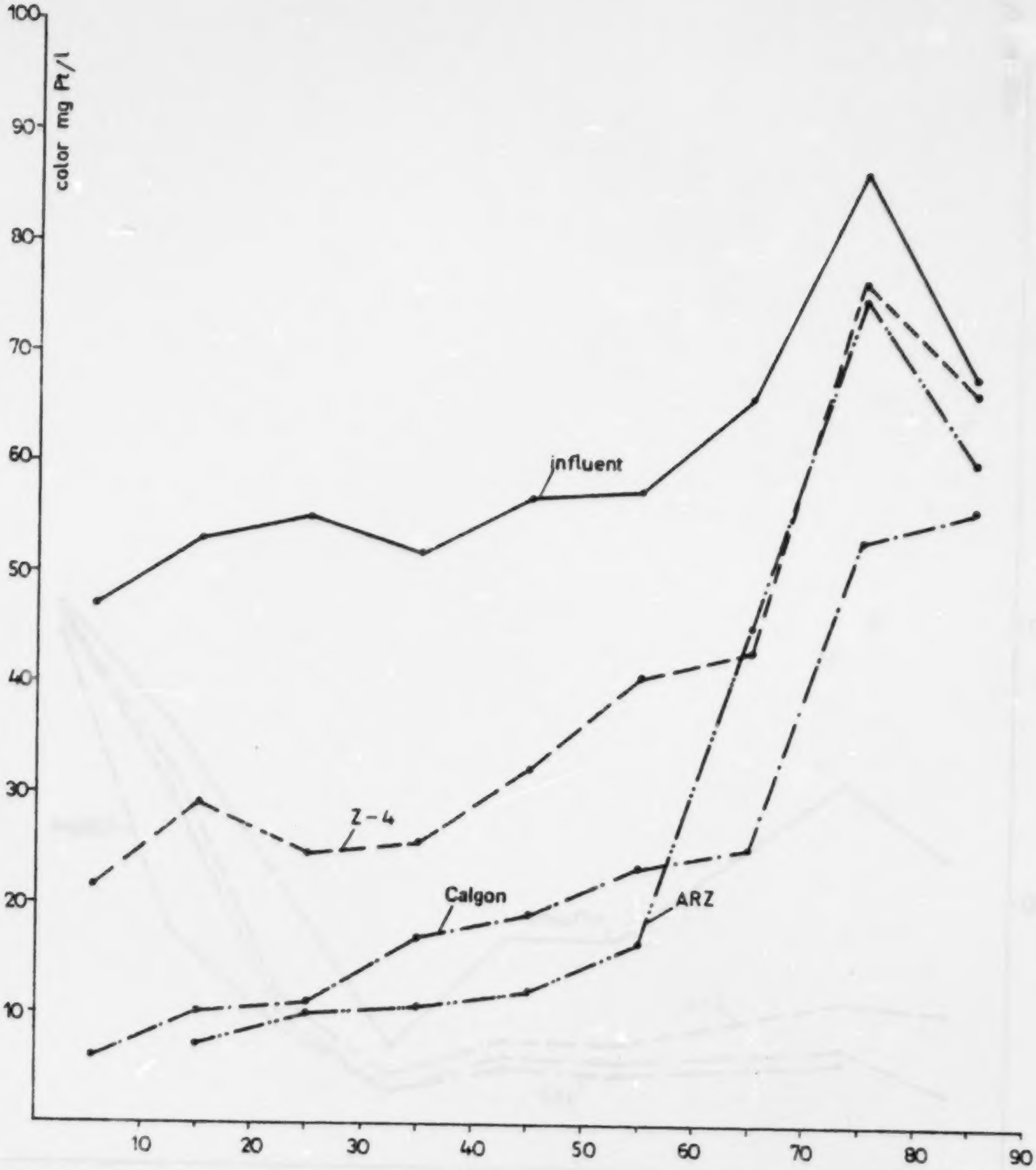

Figure 8-15. Course of color removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale.

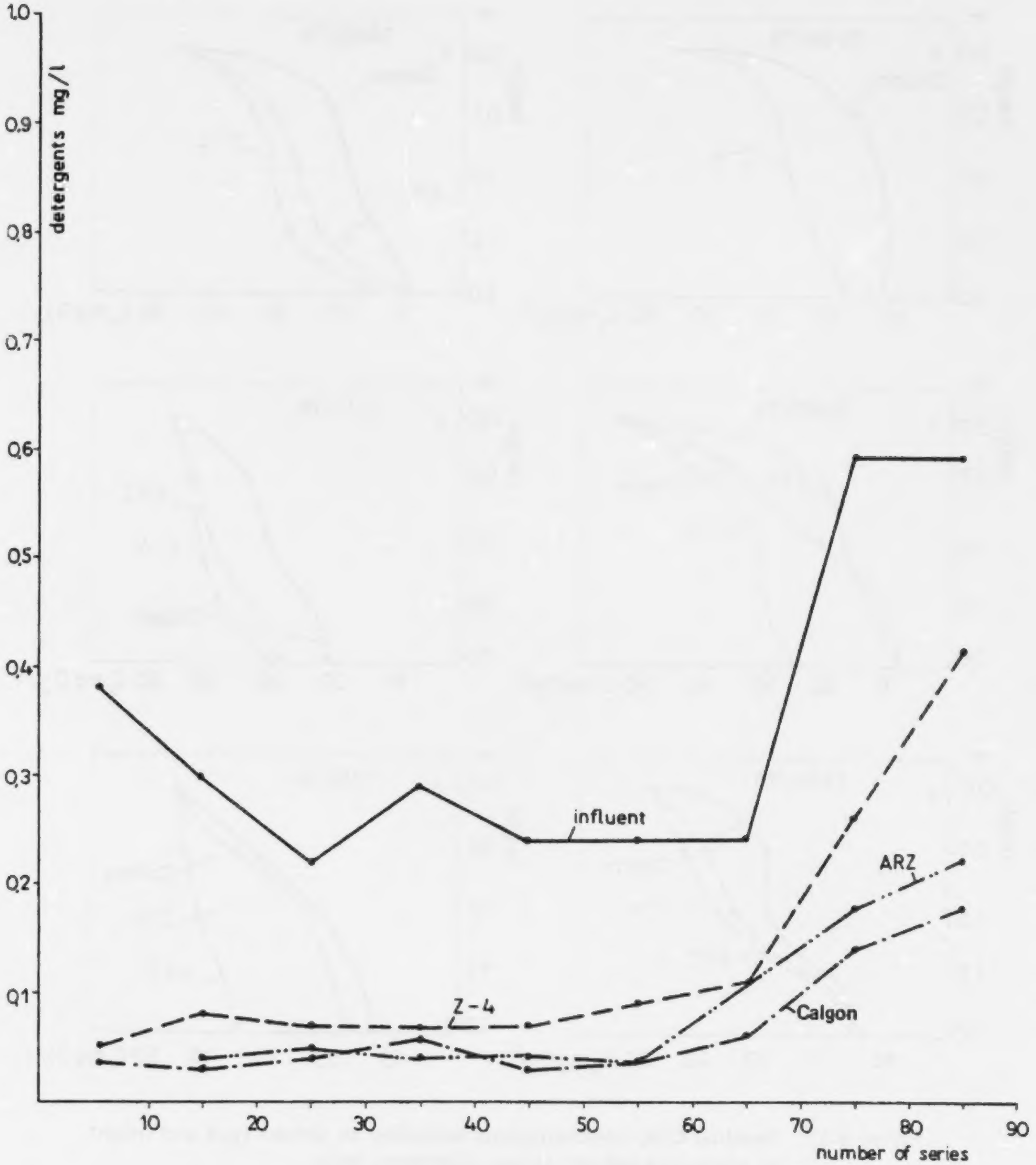

Figure 8-16. Course of detergent removal on continuous adsorption process expressed as the average values of every 10 series, laboratory scale.

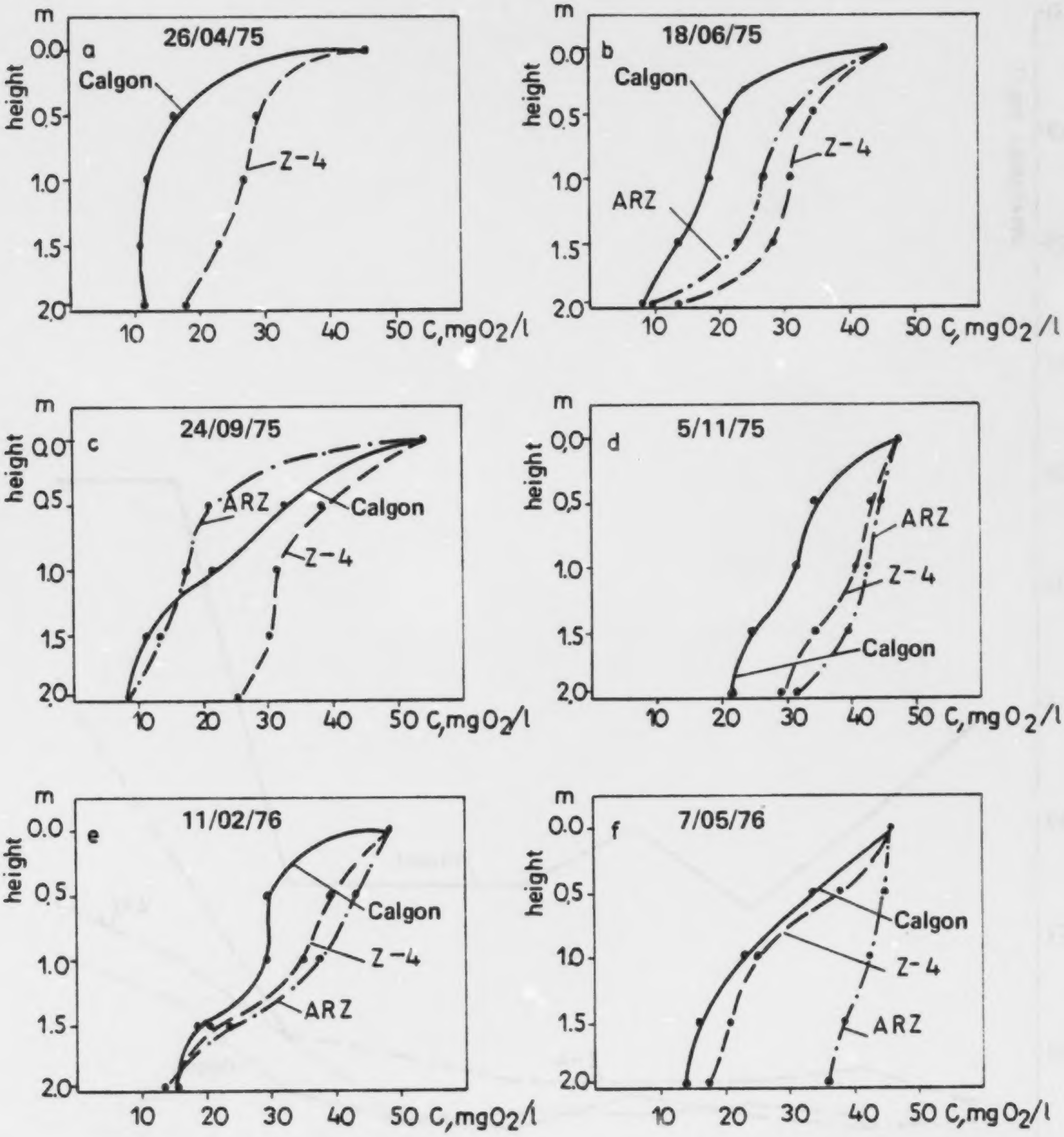

Figure 8-17. Residual COD concentrations according to carbon type and height of adsorptive column filling, laboratory scale.

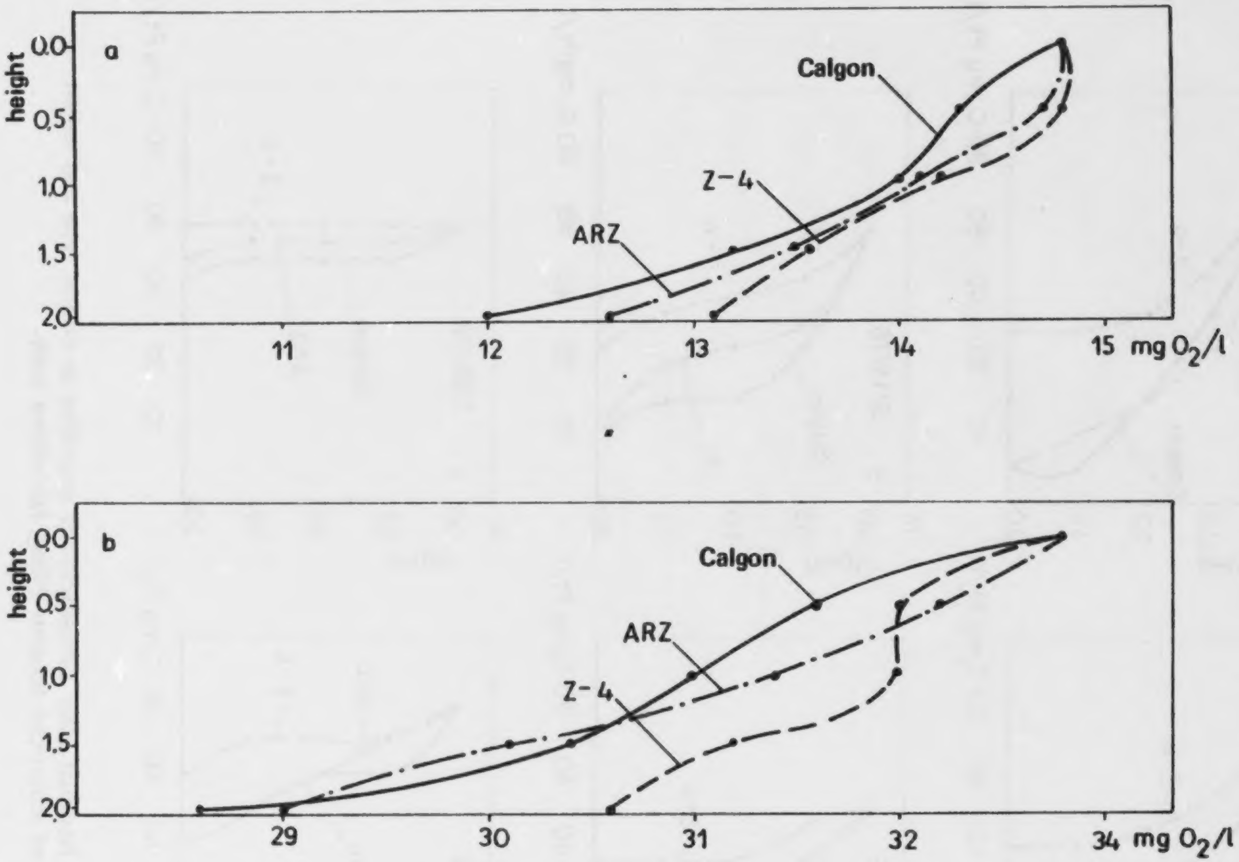

Figure 8-18. Residual BOD concentrations according to carbon type and height of adsorptive column filling, laboratory scale.

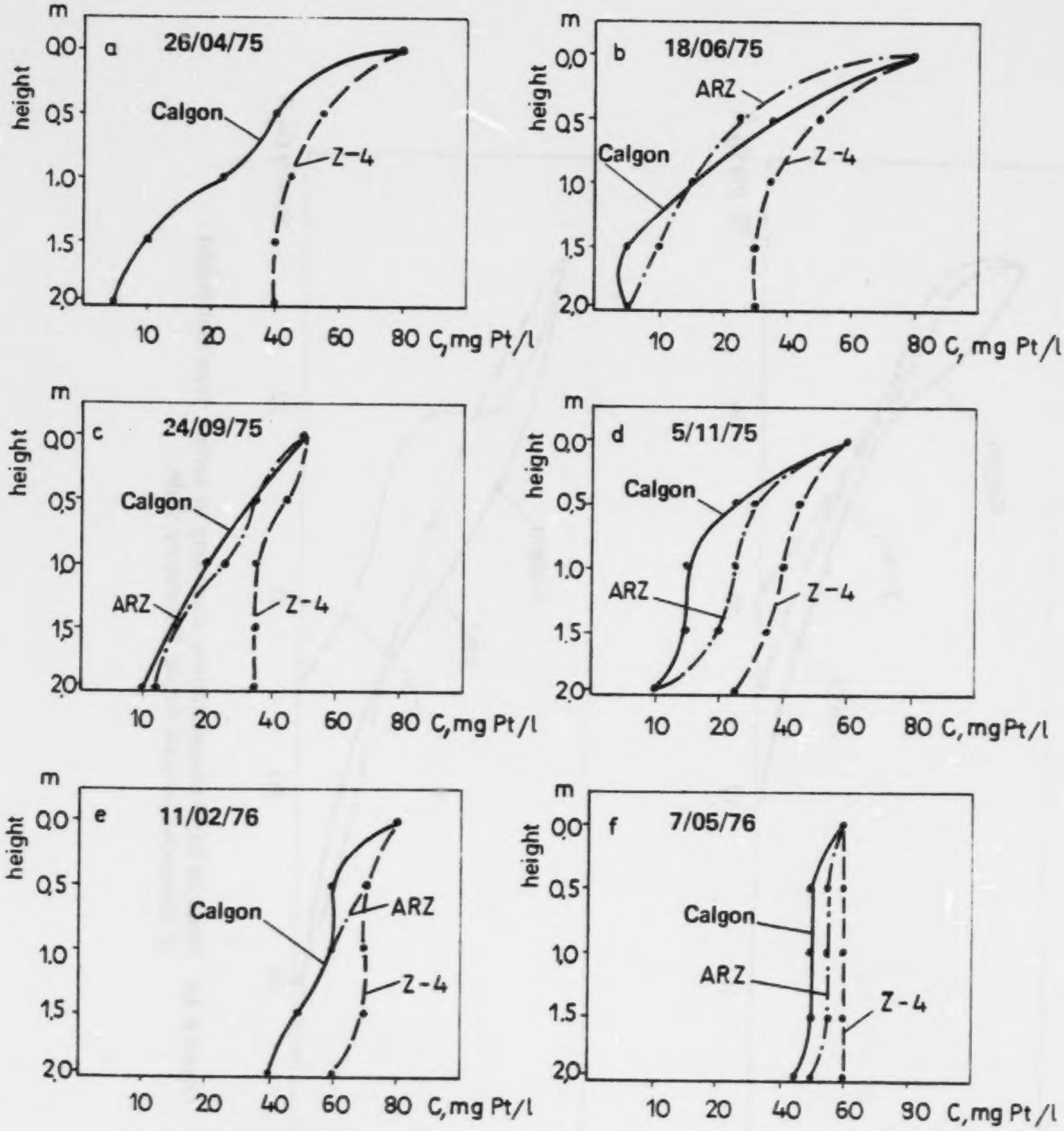

Figure 8-19. Residual color concentrations according to carbon type and height of adsorptive column filling, laboratory scale.

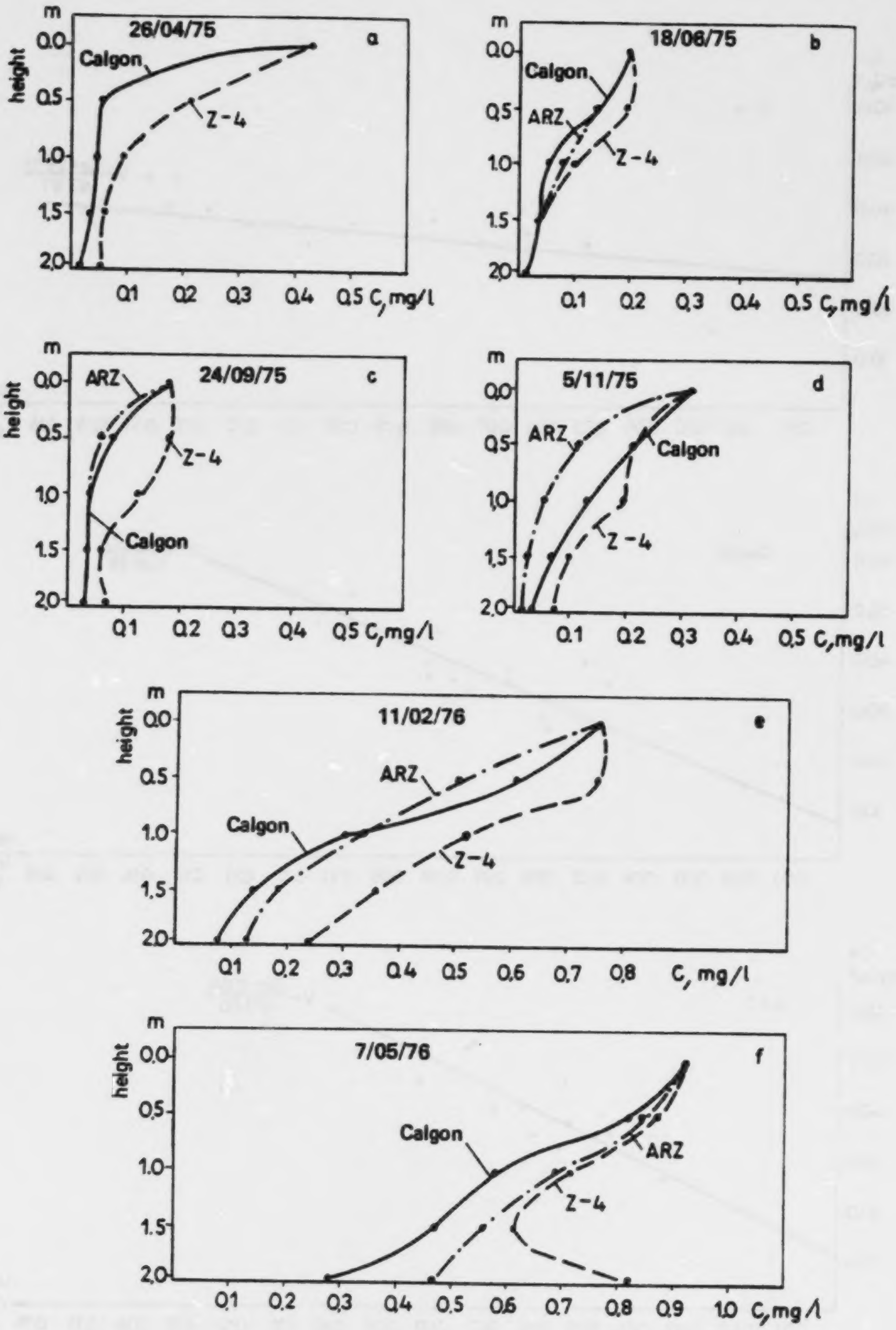

Figure 8-20. Residual detergent concentrations according to carbon type and height of adsorptive column filling, laboratory scale.

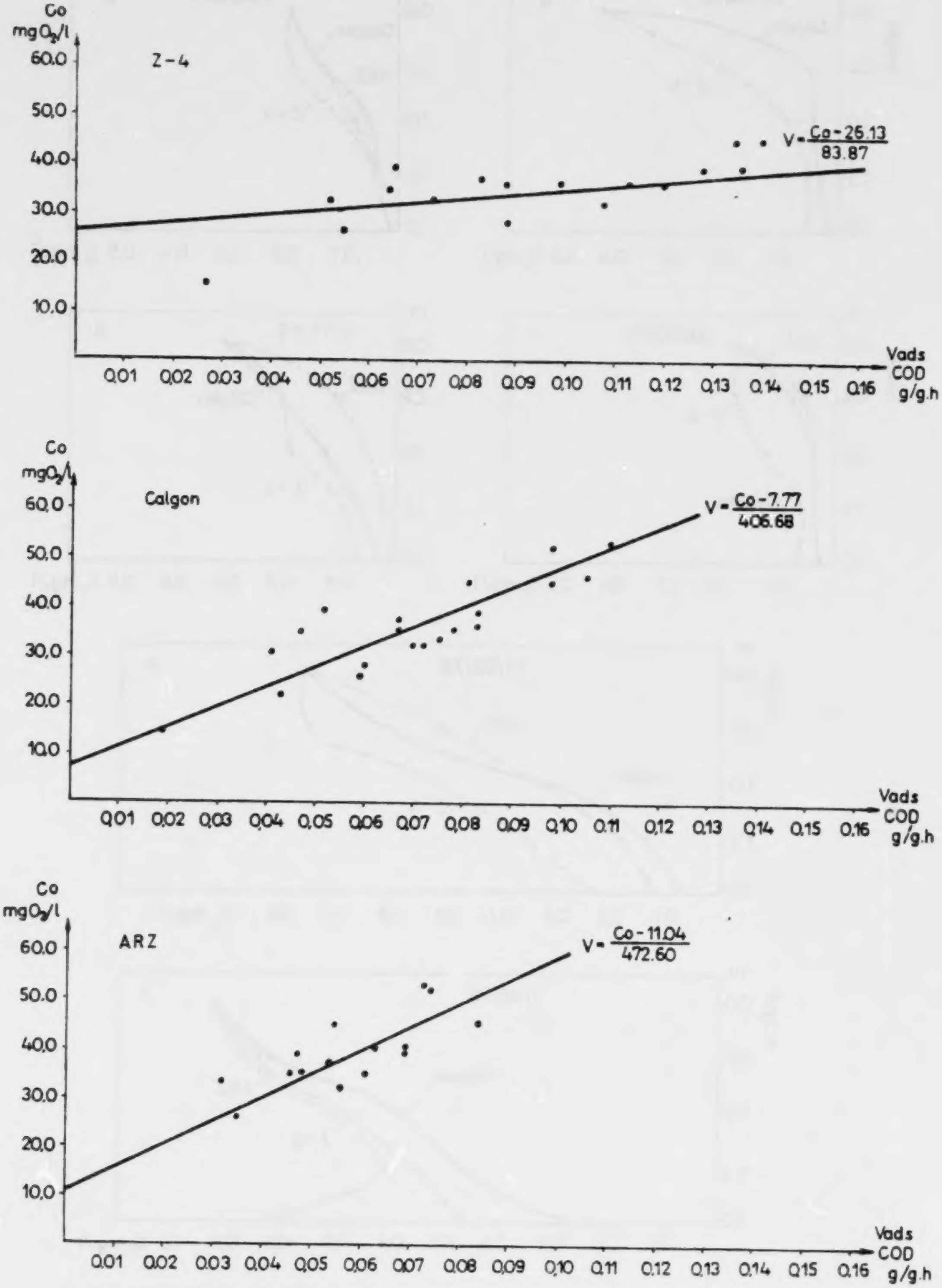

Figure 8-21. **Relation of COD absorption rate to concentration in inflow, continuous process, laboratory scale.**

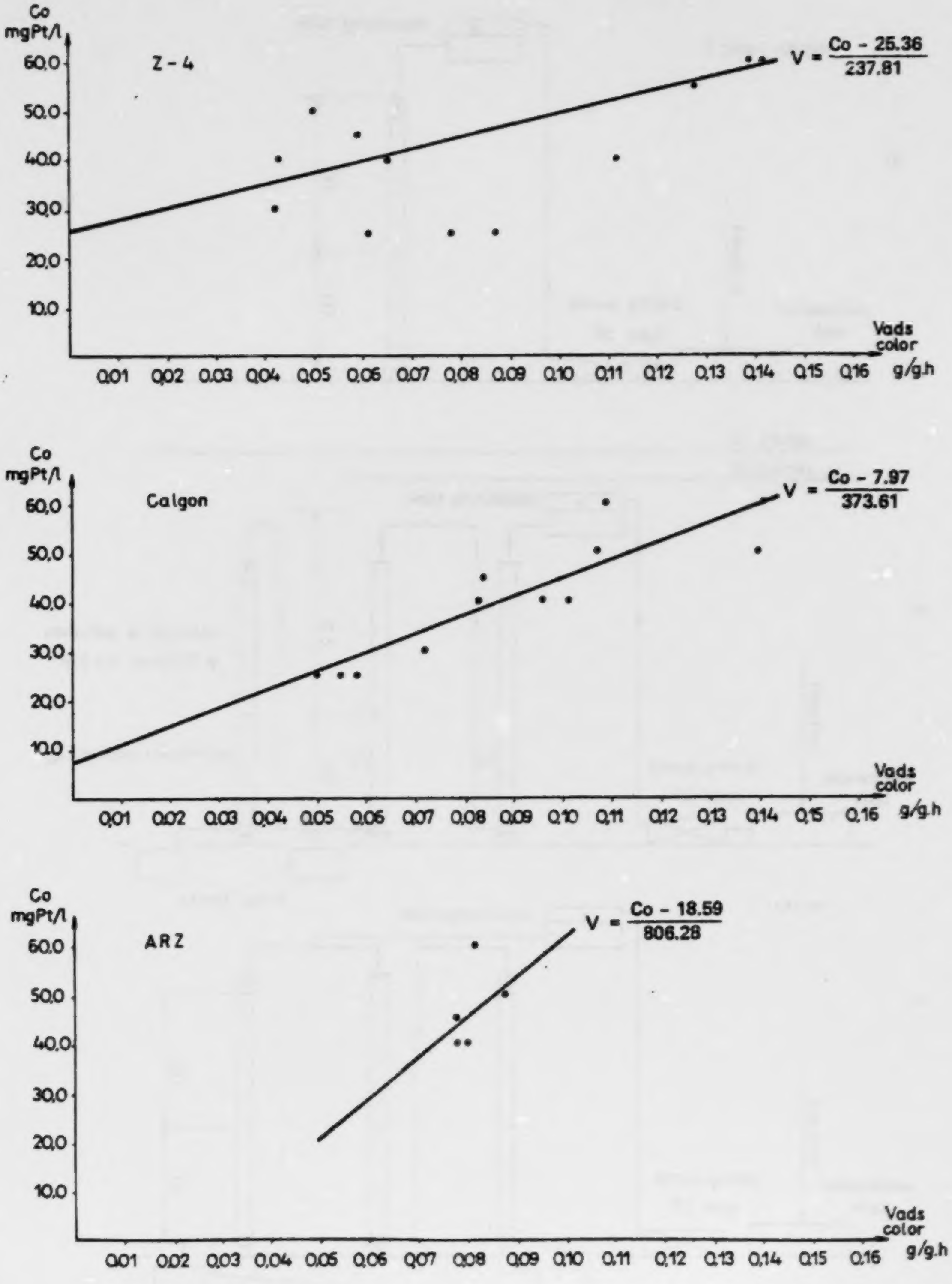

Figure 8-22. Relation of color adsorption rate to concentration in inflow, continuous process, laboratory scale.

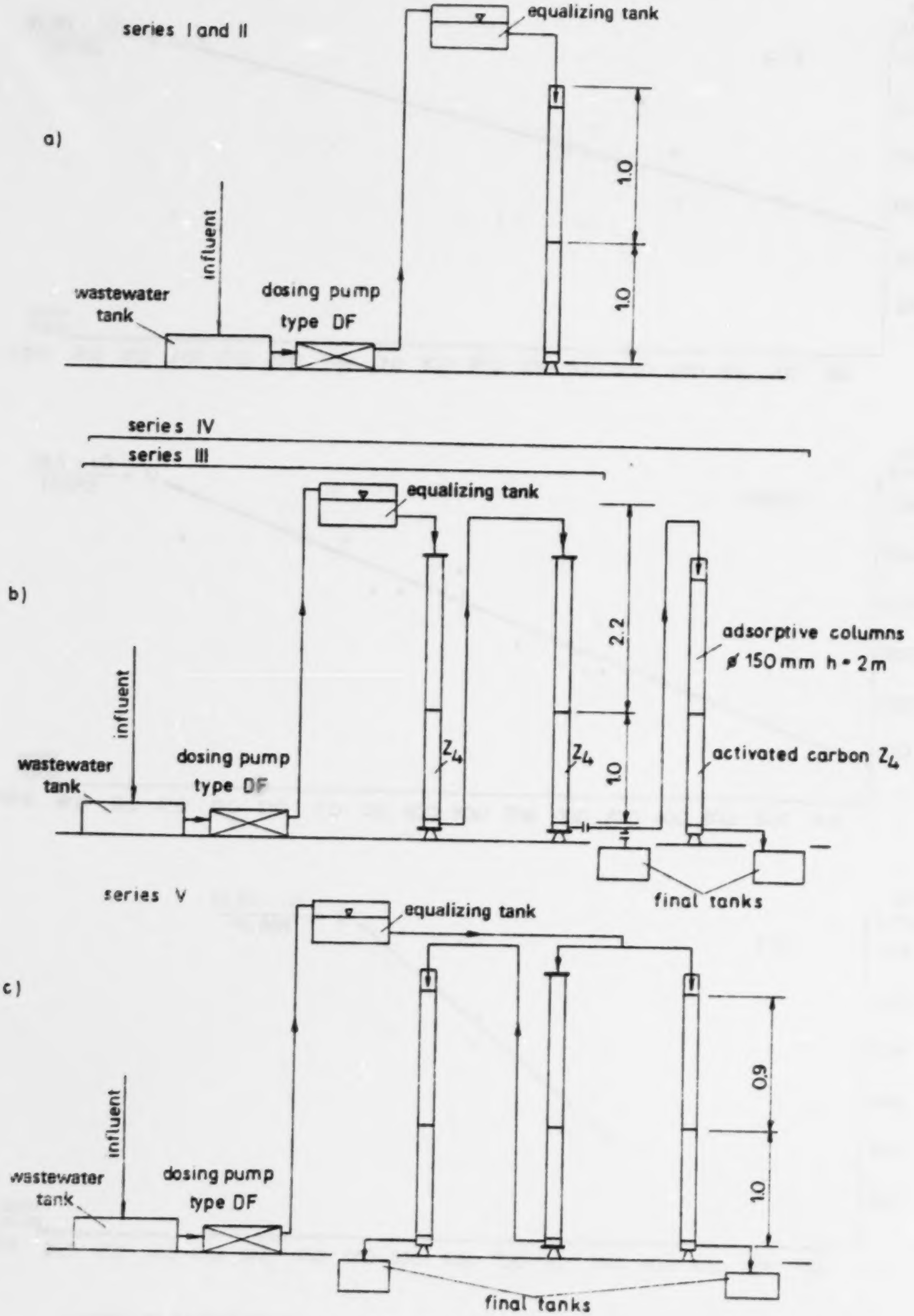
series I and II
a)
equalizing tank
influent
wastewater tank
dosing pump type DF
1.0
1.0
series IV
series III
b)
equalizing tank
influent
wastewater tank
dosing pump type DF
Z4
Z4
2.2
1.0
adsorptive columns
ø 150 mm h = 2 m
activated carbon Z4
final tanks
series V
c)
equalizing tank
influent
wastewater tank
dosing pump type DF
0.9
1.0
final tanks

Figure 8-23. Scheme of installation for studies of adsorption in a continuous system, pilot scale.

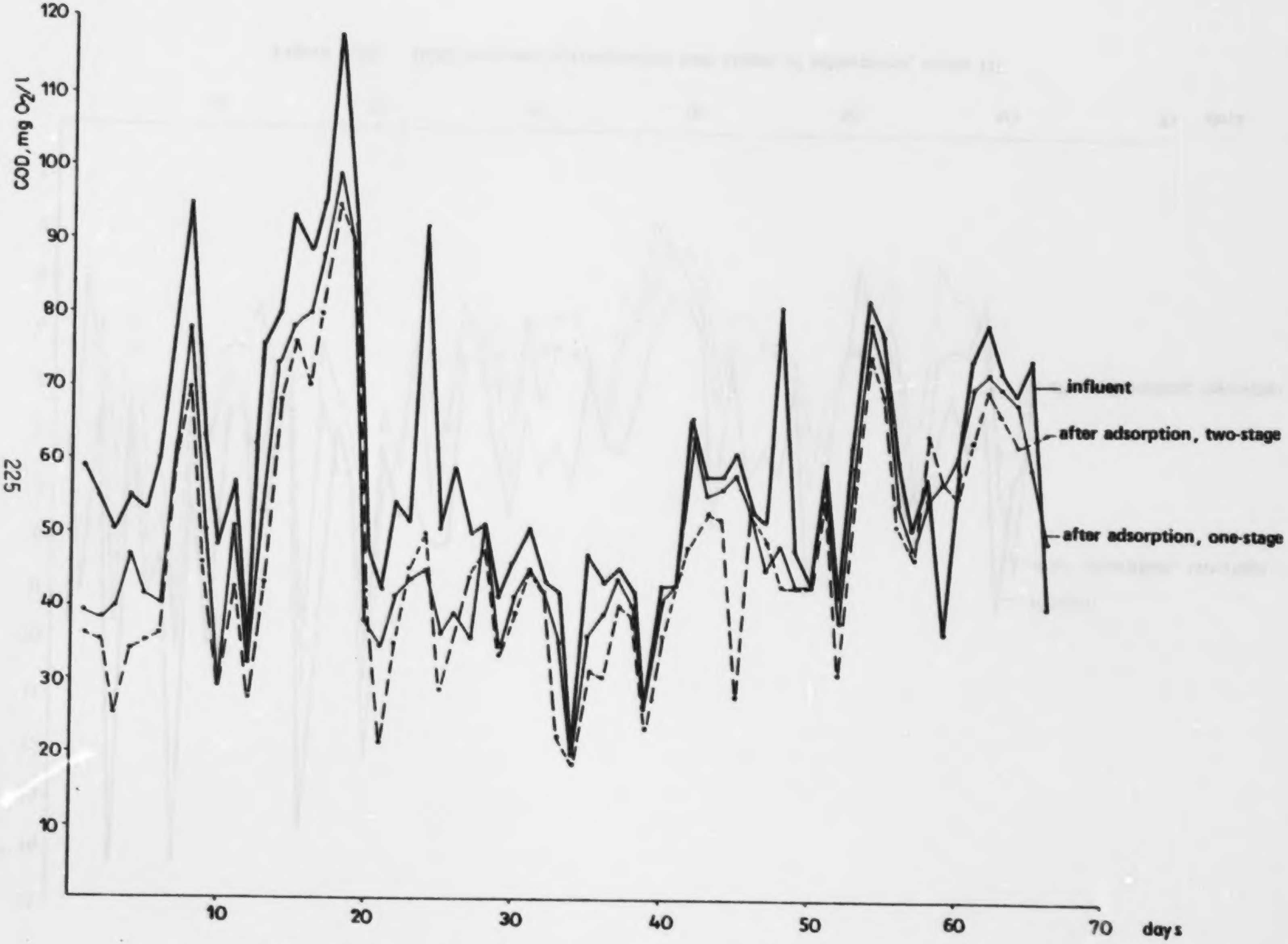

Figure 8-24. COD removal in continuous two stages of adsorption, series III.

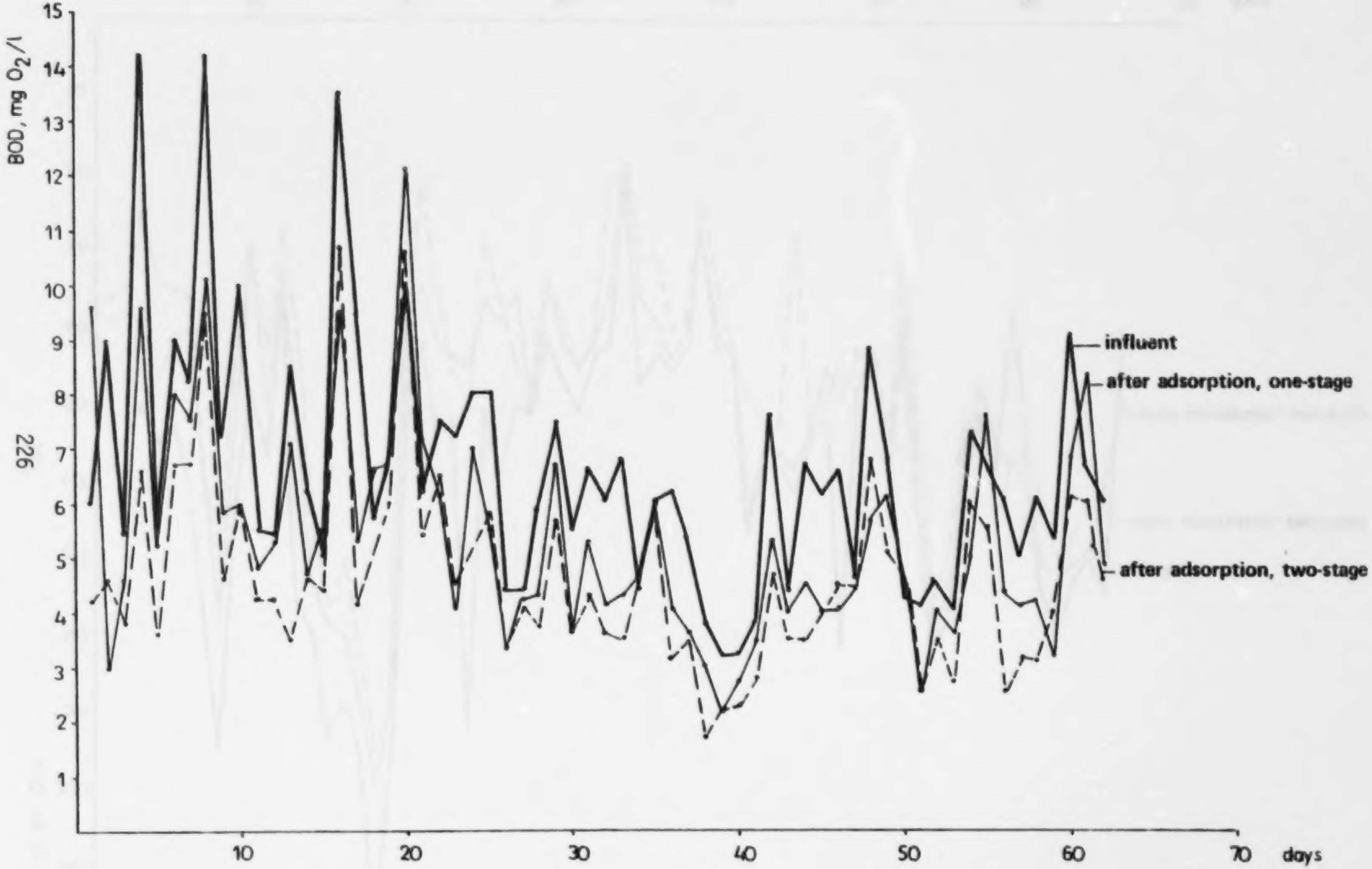

Figure 8-25. BOD removal in continuous two stages of adsorption, series III.

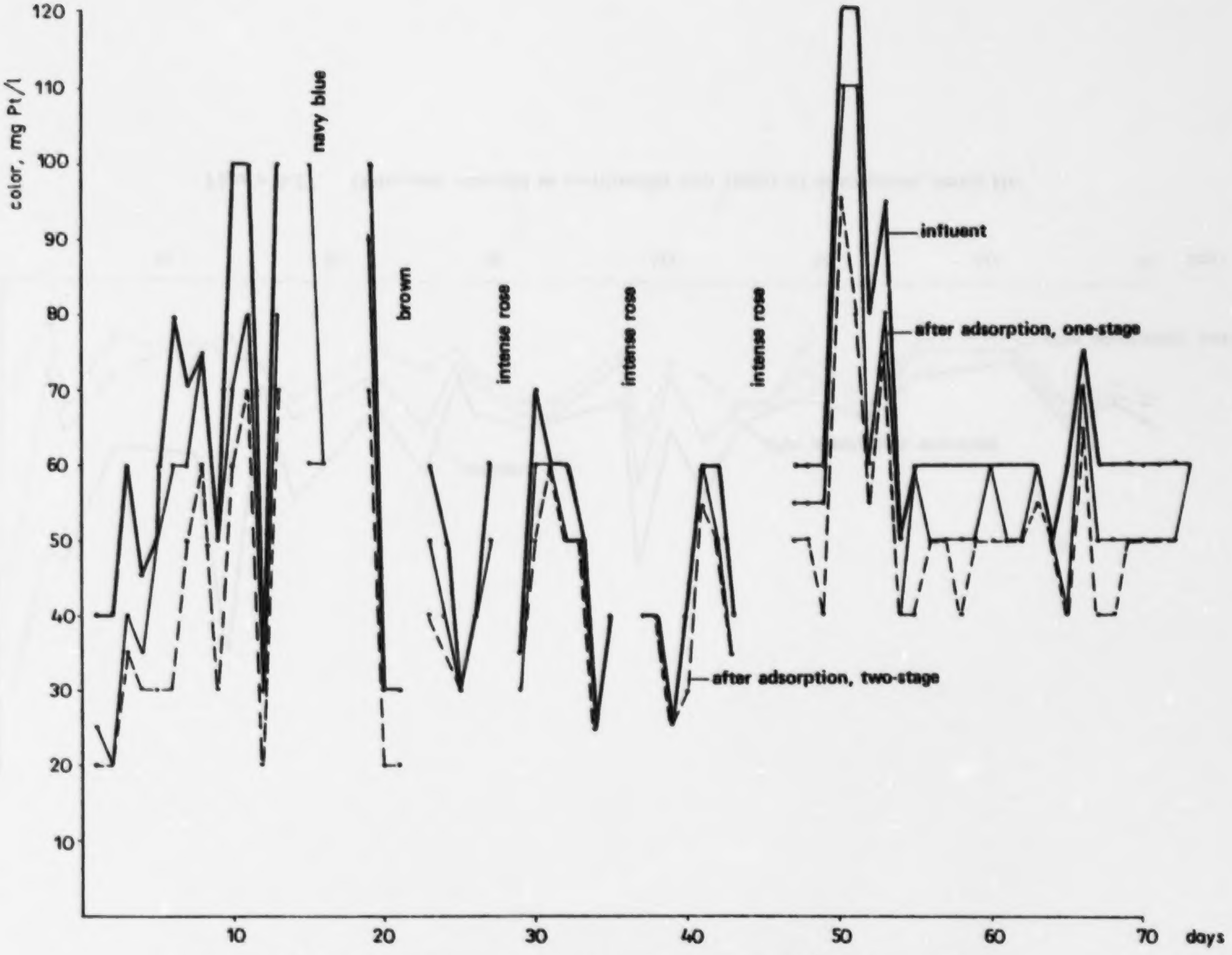

Figure 8-26. Color removal in continuous two stages of adsorption, series III.

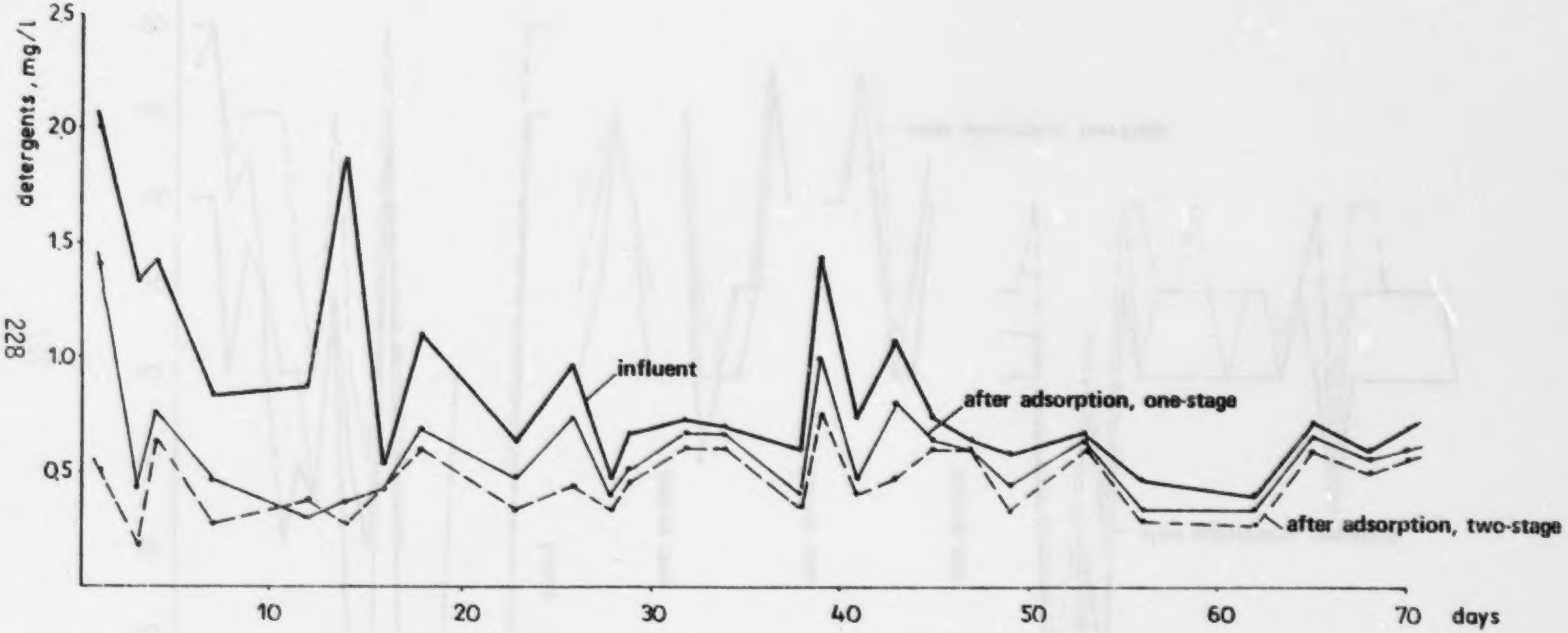

Figure 8-27. Detergent removal in continuous two stages of adsorption, series III.

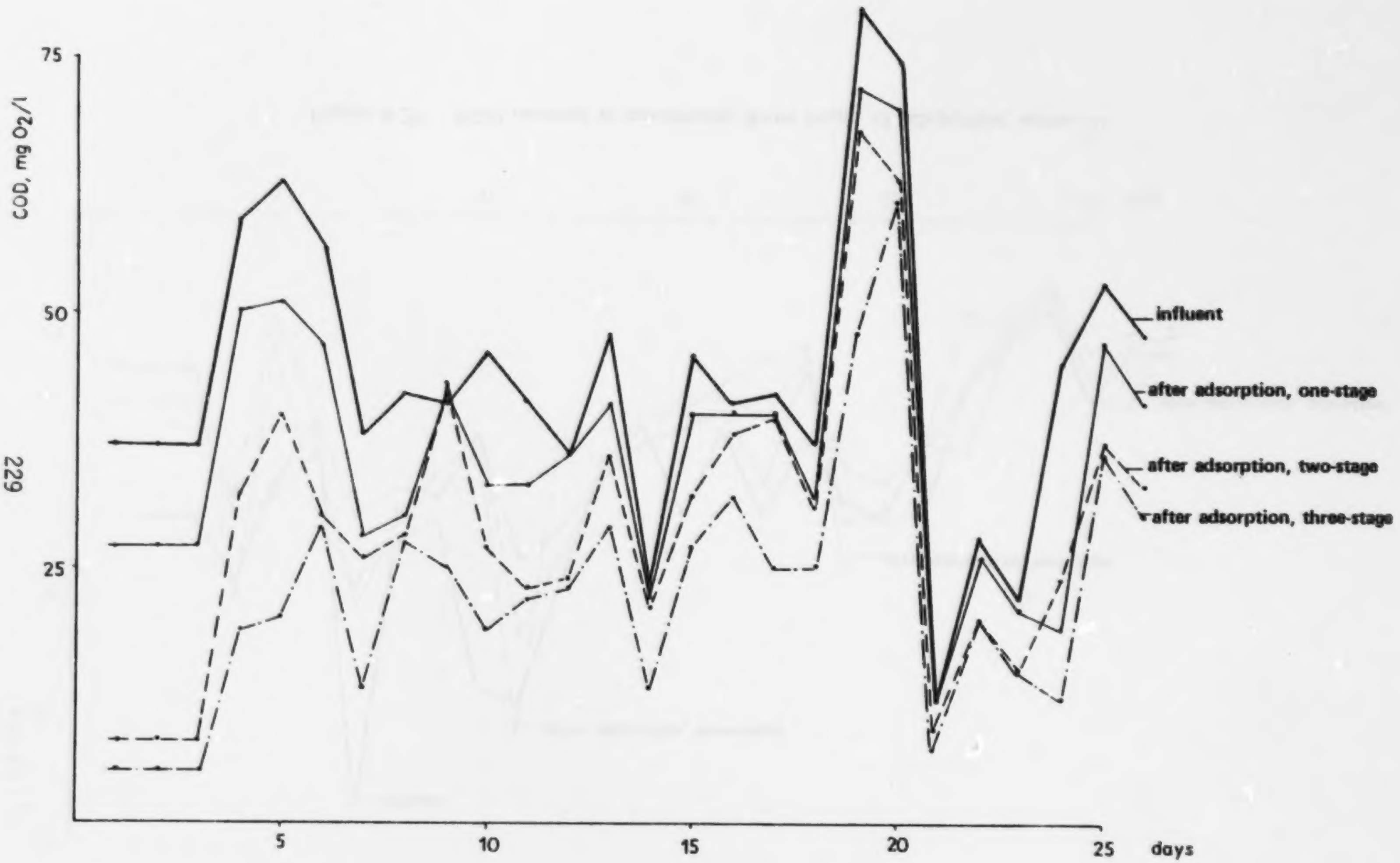

Figure 8-28. COD removal in continuous three stages of adsorption, series IV.

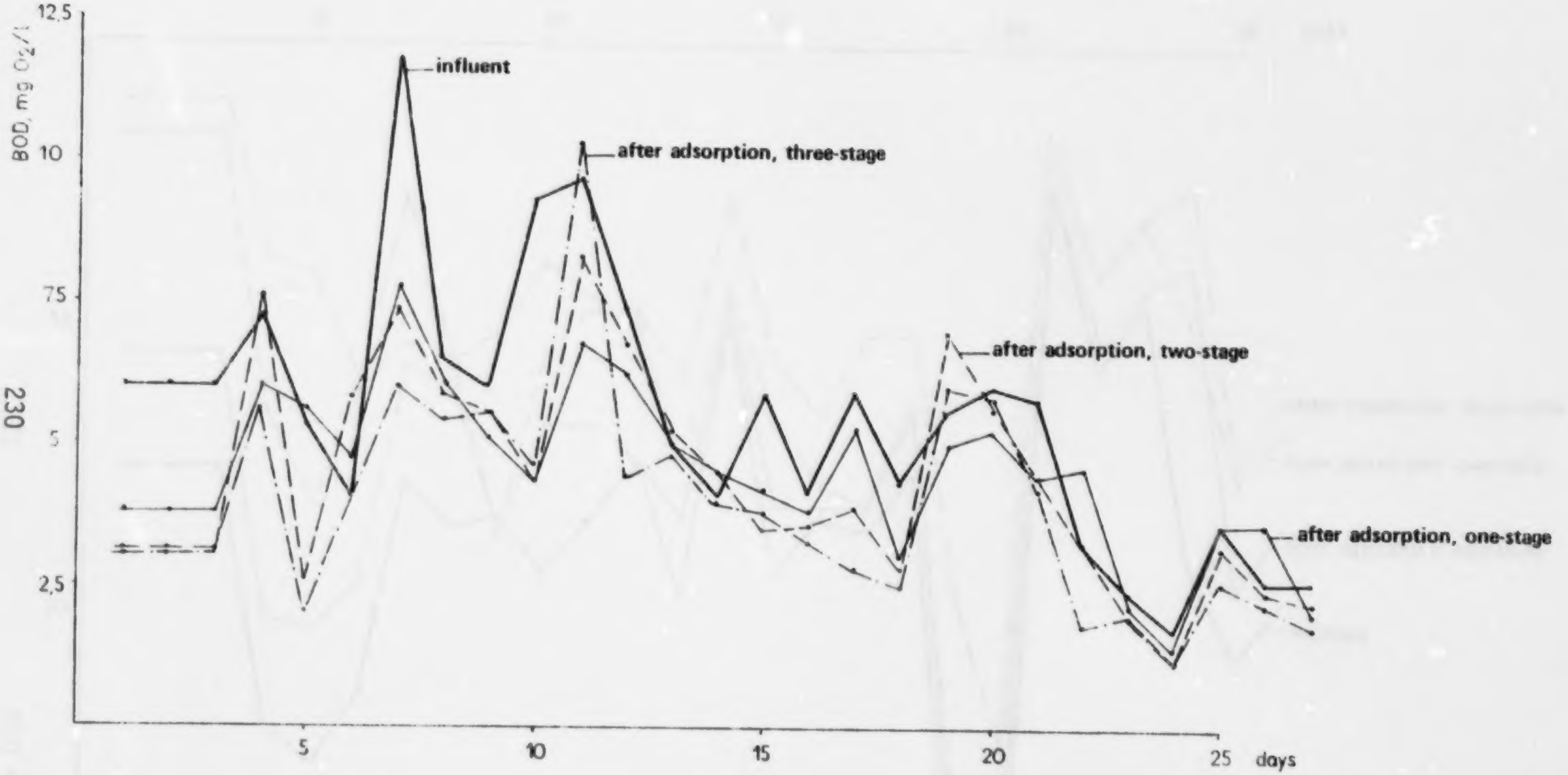

Figure 8-29. BOD removal in continuous three stages of adsorption, series IV.

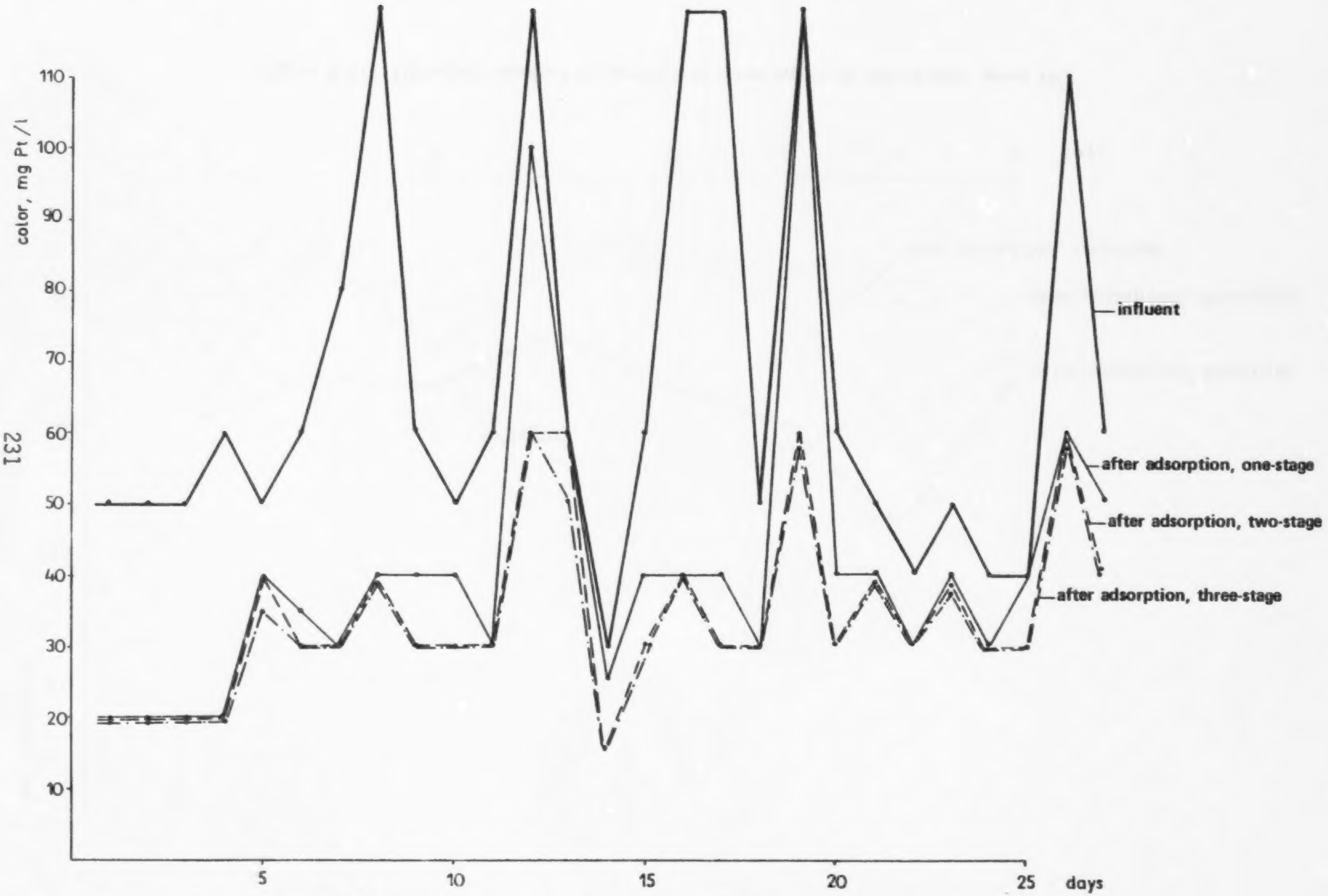

Figure 8-30. Color removal in continuous three stages of adsorption, series IV.

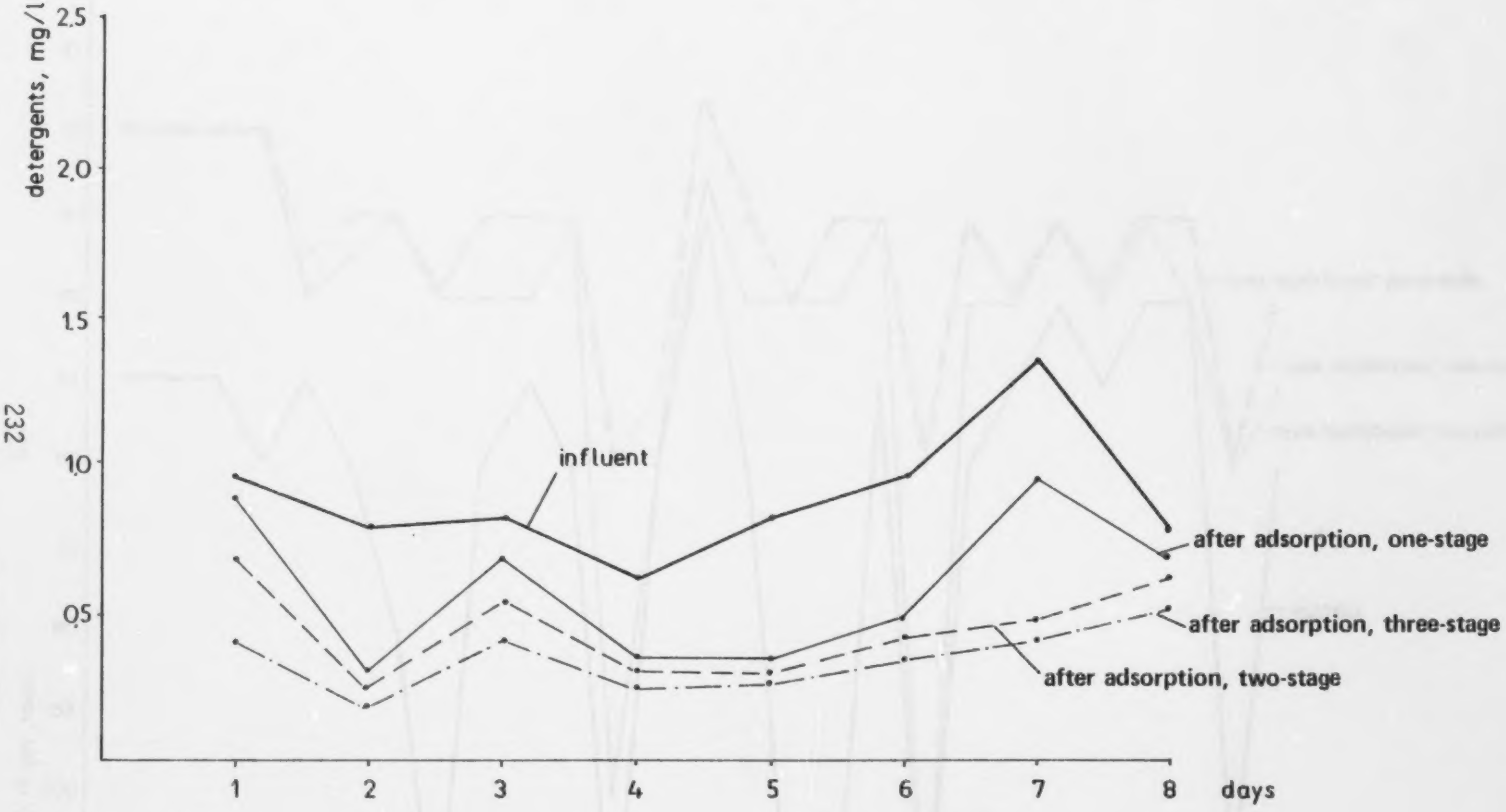

Figure 8-31. Detergent removal in continuous three stages of adsorption, series IV.

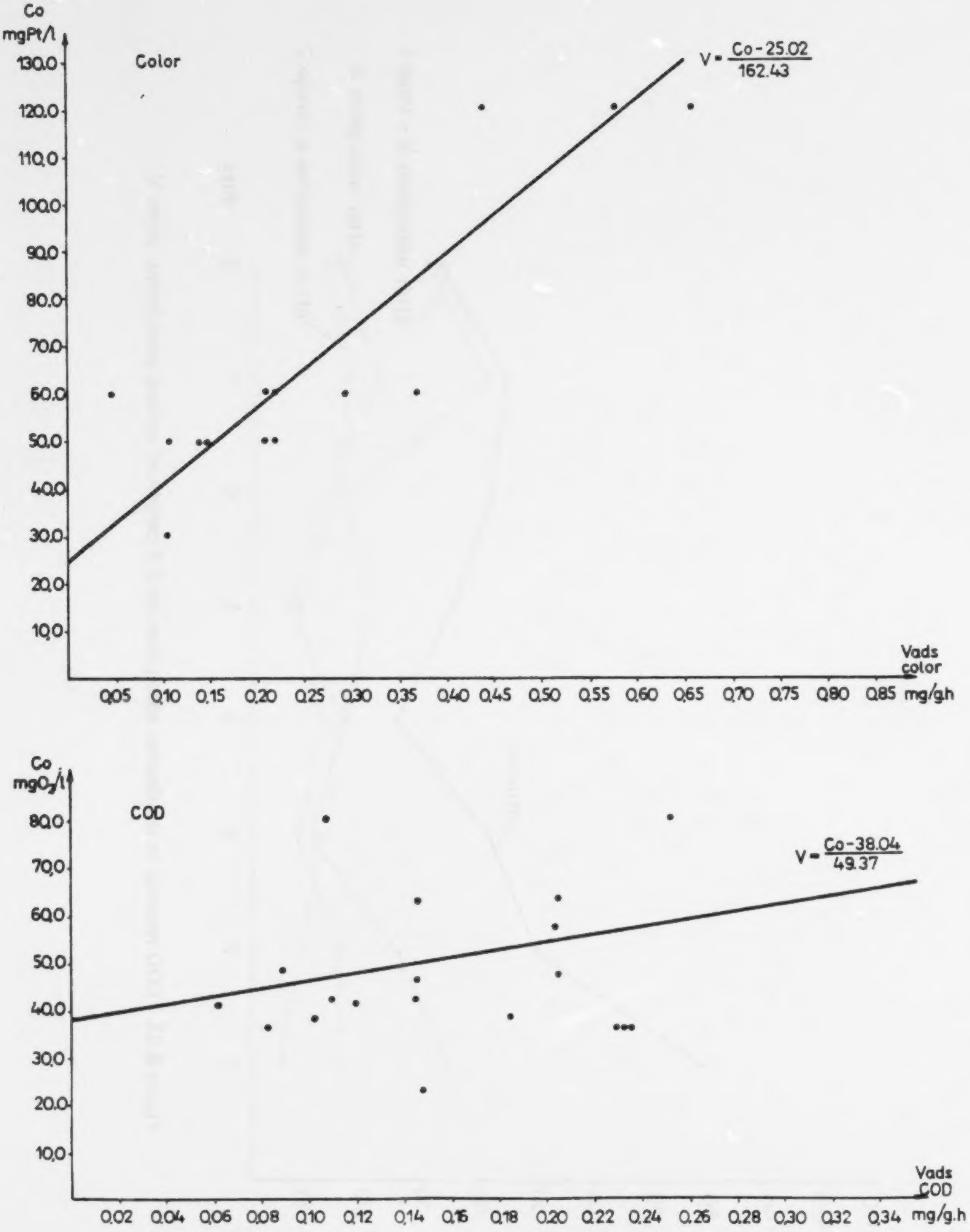

Figure 8-32. Relation of rate of color and COD adsorption to concentration in inflow, continuous process on Z-4, series IV, pilot scale.

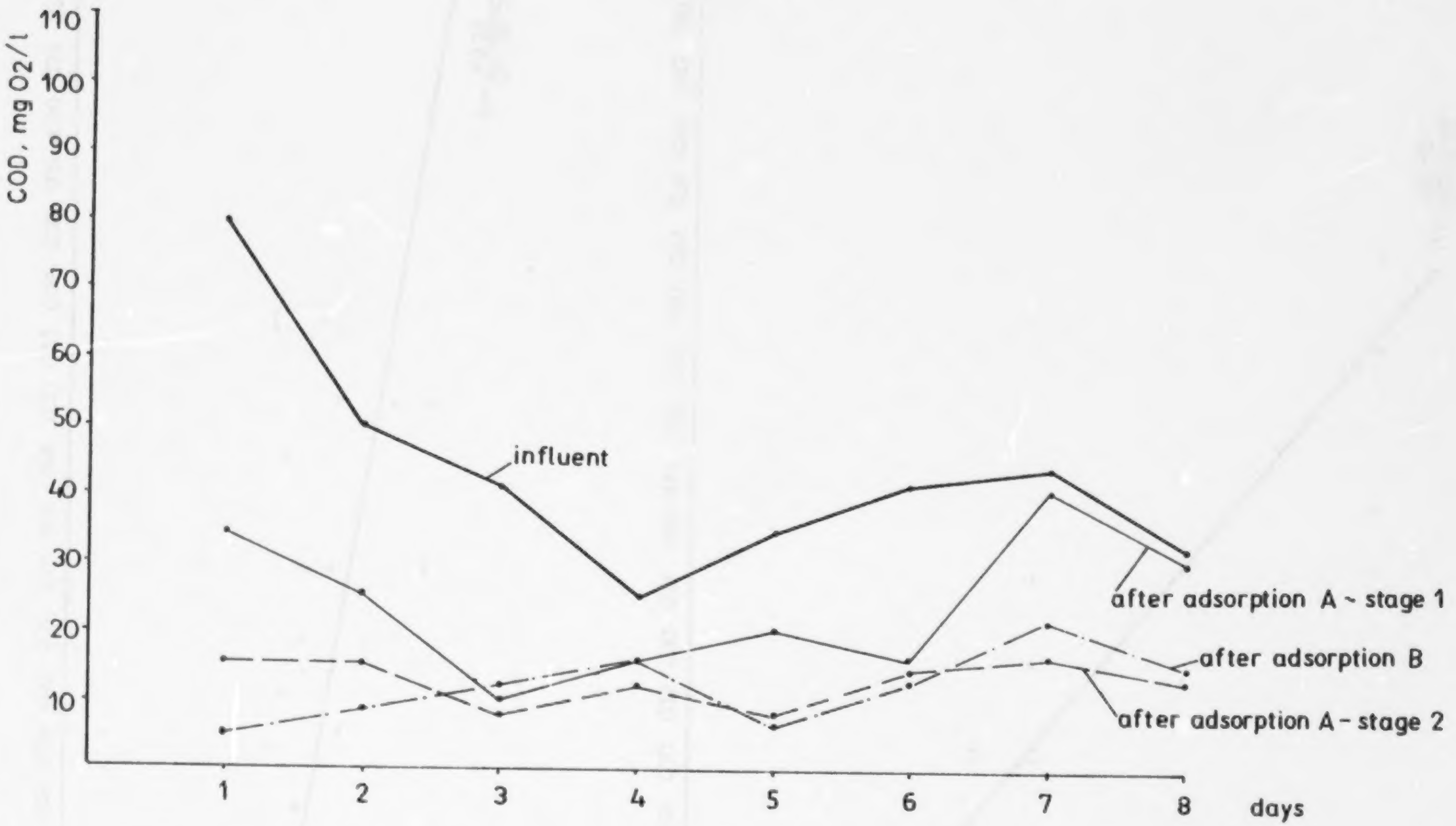

Figure 8-33. COD removal in continuous adsorption on Z-4 carbon of various granulation, series V.

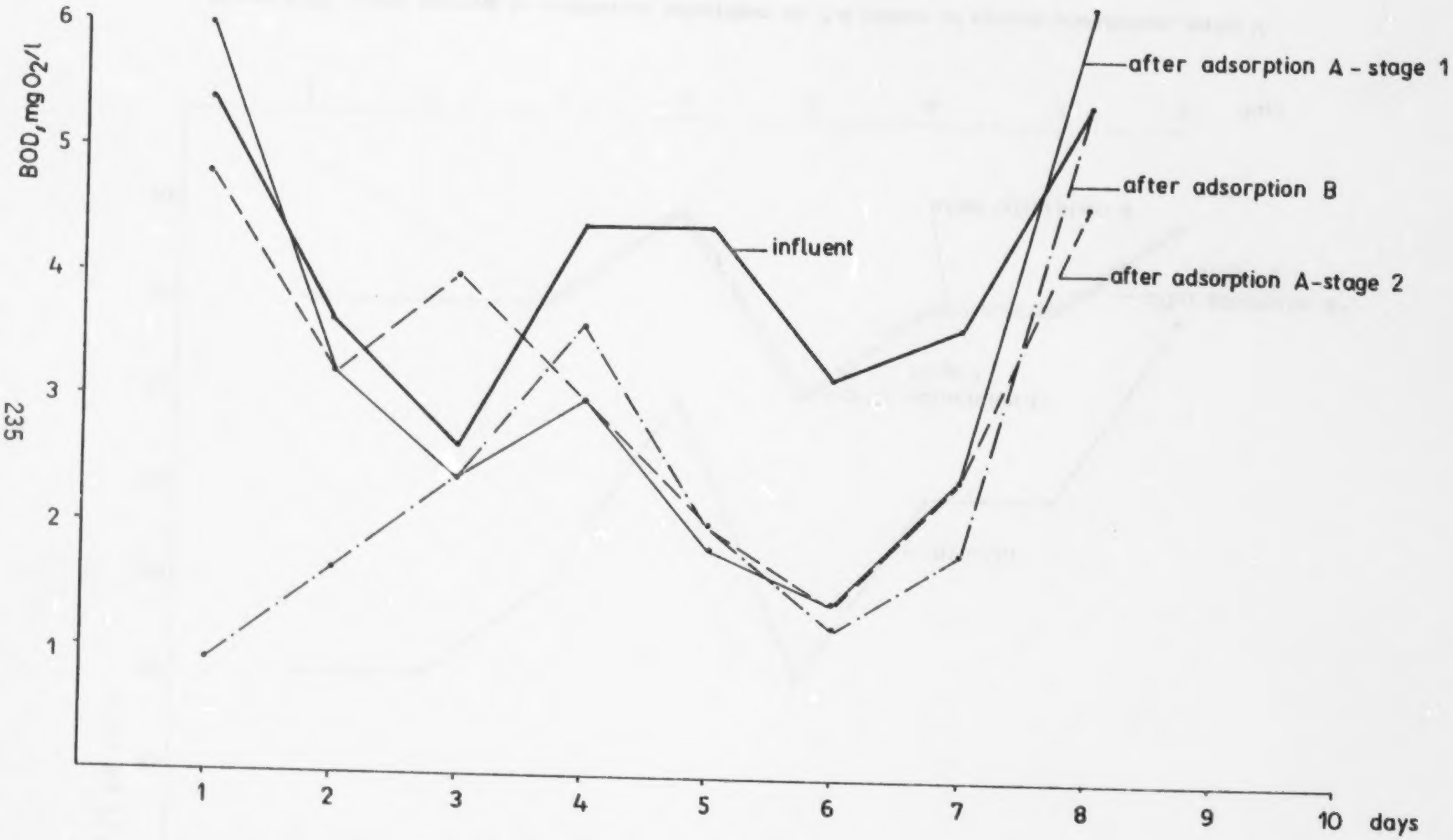

Figure 8-34. BOD removal in continuous adsorption on Z-4 carbon of various granulation, series V.

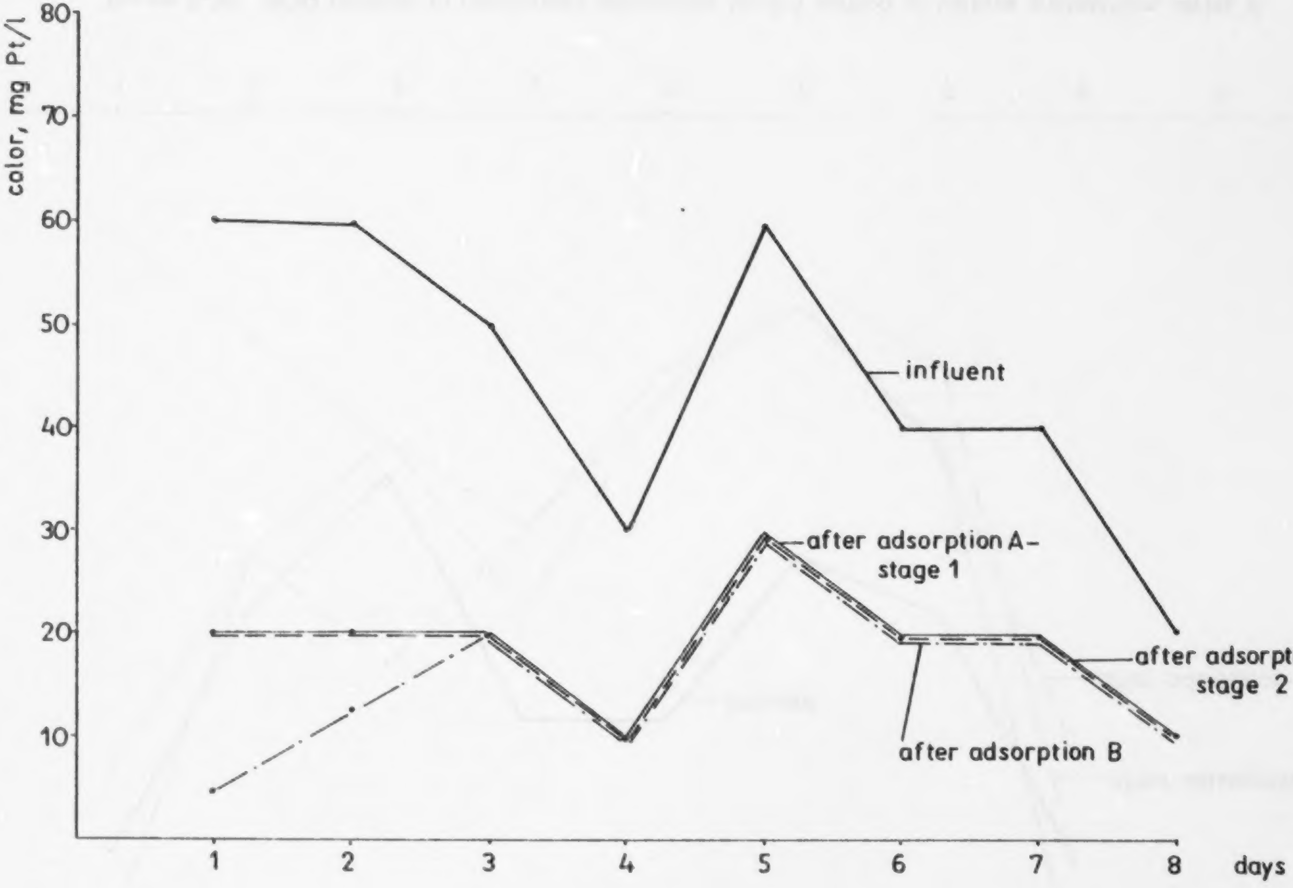

Figure 8-35. Color removal in continuous adsorption on Z-4 carbon of various granulation, series V.

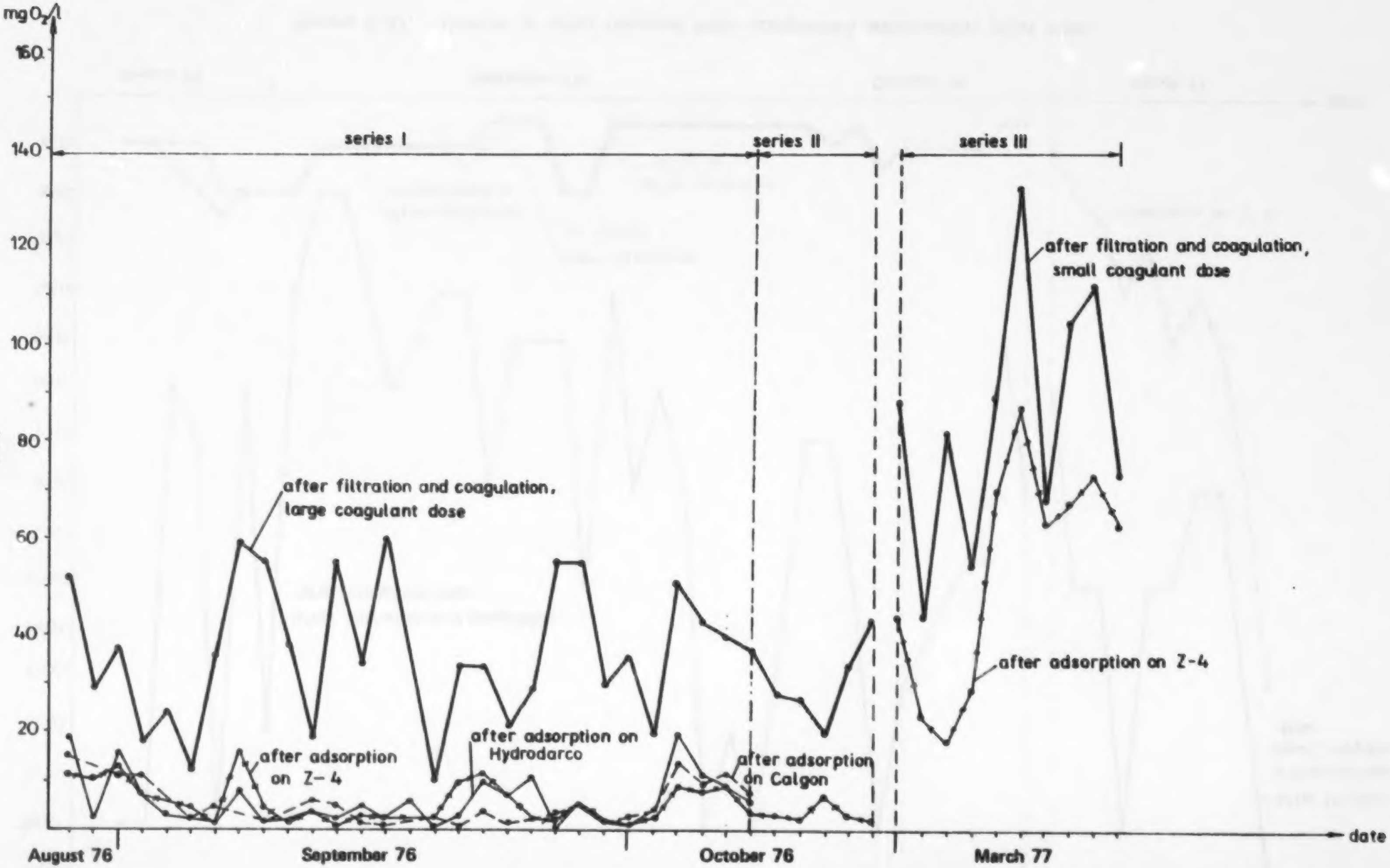

Figure 8-36. Course of COD removal from coagulated wastewater, pilot scale.

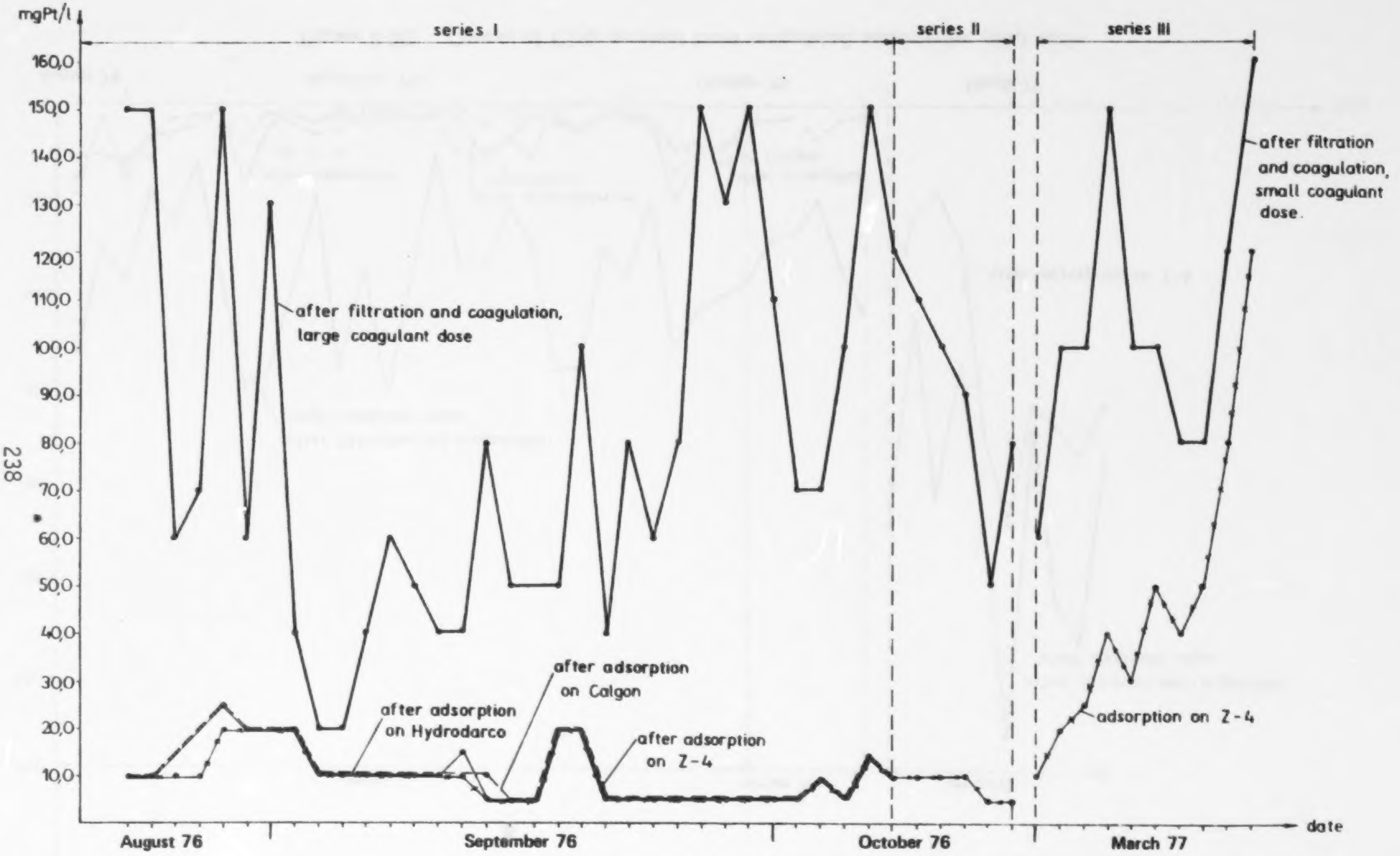

Figure 8-37. Course of color removal from coagulated wastewater, pilot scale.

Table 8-1. Physicochemical parameters of activated carbons

Carbon symbol	Means of production	Milligram number	Methylene number	Humidity	Ash content	Volatile part content	pH value	Water absorptivity	Granulation	Bulk density	Mechanical endurance	Abrasiveness	Dynamic activity min			
													Benzene	Ethyl chloride	Carbon tetrachloride	Chloropicrin
		mg	ml	%	%	%		g/g	mm	g/l	%	%				
Carbopol Z-4		371-* -470	11*	max 8*	max 7*	6.9*	10*	-	0 to 1 1 to 3 10 to 20	-	-	-	-	-	-	-
Supply I	Wood carbon activated by steam	-	9	-	4.8	6.9	-	1.3	0 to 1 1 to 3	252	-	-	-	-	-	-
Supply II		-	13	-	4.2	6.2	-	1.45	0 to 1	290	-	-	-	-	-	-
Supply III		-	31	3.0	2.5	6.5	-	2.4	0 to 1	183	-	-	-	-	-	-
ARZ	From coal on a stone base	-	36	-	21.7	-	8.0	0.72	1.53*	495	96.8	0.7	70.4	31.8	74.3	above 180
Calgon	-	-	29	-	-	-	8.0	-	0.6- -0.9	502	-	-	-	-	-	-
Hydrodarco	-	-	14	-	-	-	6.5	-	0.088- -2.5	393	-	-	-	-	-	-

*Catalog values

Table 8-2. Results of studies of porous microstructure of activated carbons

Carbon	Capillary radius r, Å														
	> 15		15 to 150		150 to 1,500		1,500 to 15,000		15,000 to 75,000		ΣΔV	Total surface area	Apparent specific gravity	Macropores	Bed porosity
	Capillary vol. ΔV														
Symbol	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	%	cm^3/g	m^2/g	g/cm^3	cm^3/g	%
Carbopol Z-4	0.1460	10.8	0.2668	19.8	0.1382	10.3	0.3864	2 28.6	0.4123	30.5	1.3487	432.6	0.655	0.078	47
Shaped ARZ	0.4600	48.3	0.1700	17.8	0.0540	5.7	0.2568	27.0	0.0116	1.2	0.9524	1,056.4	0.790	0.031	37
Calgon	0.3470	41.6	0.1789	21.5	0.1312	15.7	0.1661	19.9	0.0107	1.3	0.8339	866.9	0.800	0.043	37
Hydrodarco	0.1720	17.9	0.4020	41.8	0.1706	17.7	0.1785	18.6	0.0381	4.0	0.9612	534.8	0.731	0.055	43

Table 8-3. Comparison of adsorption effects using three kinds of activated carbon, laboratory scale investigations

Activated carbon data						COD				BOD				Detergents				Color			
								Load removal				Load removal				Load removal				Load removal	
Kind of carbon	Volume	Weight	Hydraulic loading	Contact time in empty bed	Total amount of wastewater	Average effluent concentration	Average removal	Total	Per 1 g carbon	Average effluent concentration	Average removal	Total	Per 1 g carbon	Average effluent concentration	Average removal	Total	Per 1 g carbon	Average effluent concentration	Average removal	Per 1 g carbon	Total
	dm^3	g	$\frac{dm^3}{dm^2/h}$	min	m^3/g	mg/l	%	g	g/g	mg/l	%	g	g/g	mg/l	%	g	g/g	mg/l	%	g/g	g
Z-4	759.8	217.5	1.4	42	4660	52.1	30.1	104.3	0.479	7.9	26.6	13.3	0.061	0.15	59.6	1.02	0.0047	40.7	30.4	0.381	83
Calgon	759.8	382	1.4	42	4710	41.1	45.4	161.3	0.326	6.6	38.3	19.2	0.039	0.06	83.3	1.45	0.0029	25.0	55.3	0.382	146
ARZ	759.8	471	1.4	42	4510	41.3	36.7	107.7	0.320	5.3	41.5	16.9	0.050	0.05	80.2	1.05	0.0031	23.9	57.6	0.312	147

Table 8-4. Physicochemical properties of activated carbons used in the regeneration process and of fresh carbons

Kind of active carbon	Carbons used at pilot station			Carbon used in laboratory investigations					
	Fresh Z-4-I	spent carbons		Fresh Z-4-II	Spent Z-4	Fresh Calgon	Spent Calgon	Fresh ARZ	Spent ARZ
Parameters studied		AD_1	AD_2						
Methylene number, ml	9	4	5	13	4	29	13	36	29
Ash content, %	4.8	3.3	2.9	4.2	5.6	7.2	9.0	19.8	20.0
Volatile solids, %	6.9	11.5	11.3	6.2	10.4	8.9	13.3	6.5	10.2
Water absorptivity, g/g	1.30	1.27	1.29	1.45	0.94	0.67	0.49	0.69	0.60
Bulk density, g/dcm^3	252	246	272	290	321	508	575	514	534
Humidity, %	-	-	-	7.5	10.0	8.0	16.0	9.4	15.0
Sieve analysis, %									
>1 mm	21	14	16	63.5	66.5	60.0	52.0	19.0	52.0
1 to 2 mm	77	82	82	31.5	28.5	40.0	48.0	74.0	48.0
< 2 mm	2	4	2	5.0	5.0	0.0	0.0	7.0	0
Total surface area, m^2/g	360.38	218.65	243.0	-	-	-	-	-	-

Table 8-5. Results of regeneration of Z-4, Calgon, and ARZ used in laboratory investigations by a continuous method

Process conditions: Temperature - 700° C
Regeneration time - 30 min
Regeneration of Z-4 with 300 g 0.5 dm^3/h of steam added

Kind of activated carbon after regeneration			
Parameters	Z-4	Calgon	ARZ
Methylene number, ml	12	32	36
Water absorptivity, g/g	1.20	0.60	0.70
Bulk density, g/l	308	517	500
Ash content, %	6.5	10.0	22.4
Volatile solids, %	4.2	2.6	3.4
Regeneration capacity, %	88.3	88.7	91.4
Sieve analysis, %			
> 1 mm	77.5	66.0	10
1 to 2 mm	22.0	34.0	87
< 2 mm	0.5	0.0	3.0

Table 8-6. Results of regeneration of Carbopol Z-4, spent in the two-stage adsorption process (AD_1 and AD_2)

Process conditions: Temperature 800° C
Steam used - 300 g 0.5 dm^3 carbon/h

Parameters	AD_1				AD_2				
	Regeneration time				Regeneration time				
	12	30	40	60	10 without steam	10	15	20	30
Methylene number, ml	9	14	17	19	7	8	9	12	12
Ash Content, %	3.9	4.5	5.0	5.6	3.2	-	3.6	3.5	4.0
Volatile solids, %	-	2.6	2.3	2.7	2.9	-	-	3.3	2.8
Water absorptivity, g/g	-	1.76	1.94	1.86	1.33	-	-	1.45	1.77
Bulk density, g/dm^3	265	225	215	212	270	-	248	228	225
Total surface area, m^2/g	-	482.67	459.65	455.2	369.42	-	-	440.41	447
Sieve analysis, %									
> 1 mm	10.8	14.0	9.0	9.0	17.0	-	13.6	18.0	18.0
1 to 2 mm	78.6	78.0	77.0	82.0	80.0	-	83.4	80.0	80.0
< 2 mm	10.6	8.0	14.0	9.0	3.0	-	3.0	2.0	2.0
Regeneration capacity, %	85.3	72.9	65.7	58.5	90.7	84.6	80.6	83.8	73.1

Table 8-7. Conditions of operation for activated carbon columns, pilot scale installation

Volume of one bed - 17.6 dcm^3 in dry state

		Series I	Series II	Series III		Series IV			Series V		
									Row A		Row B
Parameters	Units	Stage 1	Stage 1	Stage 1	Stage 2	Stage 1	Stage 2	Stage 3	Stage 1	Stage 2	Stage 1
Kind of carbon and supply number	-	Z-4 I	Z-4 I	Z-4 I	Z-4 I	Z-4 I	Z-4 I	Z-4 I	Z-4 III	Z-4 III	Z-4 III
Granulation	mm	0.5 to 0.7	0.5 to 0.7	1.0 to 2.0	1.0 to 2.0	0.4 to 0.7	0.4 to 0.7	0.4 to 0.7	0.7 to 1.0	0.7 to 1.0	0.5 to 0.75
Carbon weight in dry state	g	3,825	3,825	4,100	4,100	4,085	4,085	4,085	3,380	3,380	3,782
Hydraulic surface loading	m^3/m^2h	5.1	5.1	5.1	5.1	5.1 (2.6)*	5.1 (2.6)*	5.1 (2.6)*	5.1	5.1	2.52
Contact time on terms of empty bed	min	12.6	12.6	12.6	12.6	12.6 (25.2)*	12.6 (25.2)*	12.6 (25.2)*	12.6	12.6	25.2
Total time of bed operation	days	33	26	74	74	27	27	27	12	12	12
Total amount of treated wastewater	m^3	55	46	121	121						

* Values in parentheses are given for the final period.

Table 8-8. Loads removed and final pollutant concentrations in individual series of adsorption on activated carbon, pilot scale installation. (Cumulative removal percentages were calculated as the average of each individual series removal)

Series (stage)		Amount of treated wastewater per 1 g carbon	COD				BOD				Detergents				Color			
			Average concentration				Average concentration				Average concentration				Average concentration			
			Influent	Effluent	Cumulative average removal	Load removal	Influent	Effluent	Cumulative average removal	Load removal	Influent	Effluent	Cumulative average removal	Load removal	Influent	Effluent	Cumulative average removal	Load removal
		m^3/g	g/m^3	g/m^3	%	g/g	g/m^3	g/m^3	%	g/g	g/m^3	g/m^3	%	g/g	g/m^3	g/m^3	%	g/g
Series I		0.0146	73.3	60.0	18.1	0.271	8.63	6.42	25.6	0.0455	3.54	2.59	26.8	0.0058	-	-	-	-
Series II		0.0114	59.5	51.9	12.8	0.136	8.04	6.54	18.7	0.0180	4.49	2.24	50.1	0.0112	-	-	-	-
Series III	stage I	0.0515	58.8	51.5	12.4	0.244	6.63	5.37	20.0	0.0385	2.63	1.72	28.8	-0.00022	-	-	-	-
	stage II	0.0515	51.5	47.7	18.8	0.136	5.37	4.70	27.1	0.0223	1.72	1.36	41.1	0.00009	-	-	-	-
Series IV	stage I	0.00715	44.7	37.9	14.8	0.00155	6.10	4.90	18.6	0.00027	2.40	1.50	45.2	0.00021	69.1	40.9	36.1	-
3/03 to 4/28	stage II	0.00715	37.9	30.0	33.5	0.00180	4.90	4.90	21.9	-	1.50	1.20	48.9	0.00007	40.9	33.4	48.7	-
	stage III	0.00715	30.0	22.7	49.8	0.00166	4.90	4.40	28.9	0.00011	1.20	0.80	60.8	0.00009	33.4	32.7	49.5	-
Series IV	stage I	0.0137	38.3	30.7	19.8	0.00185	2.60	2.60	10.7	-	3.2	2.4	21.5	0.00017	58.0	44.0	20.3	-
4/29 to 5/07	stage II	0.0137	30.7	26.0	32.0	0.00114	2.60	2.20	16.8	0.00009	2.4	1.6	43.4	0.00018	44.0	40.0	28.7	-
	stage III	0.0137	26.0	22.7	39.0	0.00080	2.20	1.90	24.8	0.00011	1.6	1.4	52.4	0.0006	40.0	40.0	28.7	-
Series V	Row A Stage I	-	43.5	24.5	43.7	-	4.10	3.30	24.9	-	0.355	0.093	73.8	-	45.0	18.8	61.1	-
	Row A Stage II	-	24.5	13.1	67.9	-	3.30	3.20	26.6	-	0.093	0.093	73.8	-	18.8	18.8	61.1	-
	Row B Stage I	-	43.5	11.5	73.5	-	4.10	2.50	34.2	.	0.355	0.063	82.3	-	45.0	14.4	68.0	-

Table 8-9. Characteristics of carbon beds and conditions of operation used for pilot scale adsorption of coagulated wastewater

		Series I			Series II	Series III	
Parameters	Units	Column 1 ϕ = 92 mm	Column 2 ϕ = 92 mm	Column 3 ϕ = 150 mm	Column 3 ϕ = 150 mm	Stage 1 ϕ = 150 mm	Stage 2 ϕ = 120 mm
Kind of carbon	-	Calgon	Hydrodarco	Z-4 Supply III	Z-4 Supply III	Z-4 Supply II	Z-4 Supply II
Granulation	mm	0.6 to 0.9	0.088 to 2.5	0.5 to 1.0	0.5 to 1.0	1 to 3	1 to 3
Weight of dry bed	g	4,506	4,506	4,506	4,506	4,020	4,020
Volume of dry bed	dcm^3	9.0	11.5	26.4	26.4	18.4	18.4
Height of bed	mm	1,300	1,530	1,620	1,620	1,040	1,630
Hydraulic loading	m^3/m^2h	1.8	1.8	0.7	2.0	5.1	8.0
Contact time in terms of empty bed	min	45	57.5	132	44	12	12

Table 8-10. Average removal of particular pollutants on activated carbon from coagulated wastewater at pilot plant

	Series I							Series II			Series III					
	Influent	Column 1 Effluent		Column 2 Effluent		Column 3 Effluent		Influent	Column 3 Effluent		Influent	Stage I Effluent		Stage II Effluent		Cumulative removal
Parameters	conc.	conc.	removal	conc.	removal	conc.	removal	conc.	conc.	removal	conc.	conc.	removal	conc.	removal	
	mg/l	mg/l	%	mg/l	%	mg/l	%	mg/l	mg/l	%	mg/l	mg/l	%	mg/l	%	%
COD	36.7	6.1	79.4	5.9	81.2	5.0	81.8	30.9	2.3	88.7	85.2	73.8	13.0	52.2	32.8	39.7
BOD	3.3	2.2	43.5	2.0	49.0	1.9	47.3	2.9	1.48	30.4	5.9	3.7	58.5	3.3	38.5	47.8
Nonionic detergents	5.6	3.75	31.5	3.2	41.6	3.0	41.5	-	-	-	17.8	13.8	20.1	10.2	22.6	40.1
Anionic detergents	trace	-	-	-	-	-	-	trace	-	-	0.61	0.54	11.5	0.48	15.6	22.1
Color spectrophotometrically (average absorption)	0.161	0.033	78.4	0.034	78.5	0.035	83.6	0.087	0.016	80.2	0.15	0.13	21.8	0.10	26.1	33.9
Color (Pt units)	84.7	11.3	78.8	10.3	80.3	9.7	83.5	88.0	9.8	91.2	105.0	79.0	31.5	46.5	41.4	46.4
TOC	17.9	4.7	73.2	6.3	63.4	6.1	65.8	15.1	6.3	56.6	41.5	32.9	20.7	26.3	20.1	35.7

SECTION 9

OXIDATION BY OZONE

INTRODUCTION

Description of the Problem

The ozonation process is at present used on a broad scale in many countries, mainly in waterworks, but sometimes as a treatment for industrial wastewater and as a tertiary treatment for municipal wastewater.

Through ozonation a number of effects can be achieved, such as [53]:

- Decomposition of hydrocarbons and other substances that cause both natural color originating from iron and manganese ions, humus and peat materials, and artificial color produced by synthetic dyes;
- total decomposition of phenol;
- removal of detergents;
- decrease of BOD and COD; and
- additional oxygenation of water.

Ozone is a gas with a water solubility of about 8 mg/l at 20° C [54]--about one-tenth the solubility of oxygen. The solubility of ozone in wastewater is 10 to 30 percent lower than in clean water [55]. Mixing the ozone-air mixture with water or wastewater results in the dispersion of very small bubbles of ozone and air directly into the layer of water, which insures the conditions for the best possible contact of gas and water. The volumes of the bubbles increase as they move from the bottom to the top in the contact chamber because of reduced pressure. The concentration of ozone in the bubbles decreases as they rise. For optimum utilization, by the time the bubbles reach the surface of the water, all the ozone should be absorbed by the water.

In accordance with the equation of mass transfer, the amount of gas absorbed is directly proportional to the bubble surface area and time of contact of phases taking part in the reaction. Therefore, the maximum contact of water with the ozone-air mixture is essential. The transmission of ozone contained in the bubbles to the water is not total because ozone undergoes decomposition, and in addition, the bubbles leaving the contact chamber still contain part of the unreacted ozone. Ozone is a reactive gas; its decomposition to oxygen takes place within 20 to 30 min. As a result, measurements of ozone solubility and reduction are difficult and liable to error. Increasing the pH of the medium does increase the rate of ozone reduction.

Description of the process

The application of ozone for wastewater treatment is based on its oxidizing properties in reactions with mineral, organic, and microbial pollutants. Ozone is distinguished by many merits in comparison with the considerably weaker oxidizing agents used hitherto. An important aspect of ozonation is that, since ozone is reduced to oxygen, the water environment does not become polluted by byproducts resulting from reduction of the oxidizer.

From the research published [53,54,55,56,57,58,59], it is clear that in municipal wastewater biologically treated and then submitted to ozonation with doses within very broad limits of concentrations from 10 to above 50 mg/l of O_3, it is possible to obtain a 50 percent decrease of organic substance content expressed by COD. As a result of the large losses, COD removal occurs very slowly when the large consumption of ozone is considered. The best COD removal effects are obtained at higher concentrations of ozone and at a higher initial COD concentration. [54,55,57]

Theoretical calculations [55] lead to the conclusion that all the COD should undergo oxidation in the ozonation process. In practice, part of the COD is resistant to oxidation, so that removal above 50 to 70 percent requires a very long contact time with the ozone. This is economically impractical.

Total organic carbon (TOC) is also only partially removed by the ozone, and a certain small part of it is resistant to oxidation [57].

From the investigations carried out on the reduction of anionic detergents in oxidation with ozone [54], it is clear that the percentage of detergent removal is high (up to 90 percent), and as in the case of the COD indicator, depends on the concentration of ozone fed in and on the contact time.

OBJECTIVES

The aim of the present investigations was:

- To determine the degree of usefulness of ozone oxidation for treatment of textile wastewater pollutants as regards removal of color, detergents, and other organic compounds expressed by the COD test;
- To check the effectiveness of the wastewater ozonation process on the pilot scale in connection with other treatment processes; and
- To establish the guidelines, conditions, and parameters for carrying out the ozonation process.

SCOPE OF INVESTIGATION

The investigations were carried out in both static conditions and dynamic conditions with continuous flow. The ozonation process in static conditions was conducted on a laboratory scale in a batch system. The batch investigations included:

- Ozone oxidation of water solutions of single dyes with known concentrations chosen from different dye groups,
- Oxidation of individual dyes with known concentrations, which were fed to the treated wastewater by the activated sludge method,
- Oxidation of mixtures of dyes with known concentrations in a wastewater environment, and
- Determination of the dependence of color removal by ozone oxidation on the concentration of dyes fed to the wastewater.

In dynamic conditions in an experimental, continuous system, the ozonation process was first of all checked on the laboratory scale in a cocurrently operating column. For the pilot scale, two variants of model system with continuous flow were applied: a one-stage system with one column operating countercurrently; and a double-stage system containing two columns, the first of which operated countercurrently, the second cocurrently.

The investigations were carried out at the pilot station in Andrychow. The wastewater used was mixed two parts industrial wastewater to one part municipal wastewater, biologically treated, and then filtered through a sand bed. Variable concentrations of ozone in the range from 9.0 to 74.6 mg of O_3/l of wastewater, and time for retaining the wastewater in the column varying from 15 to 50 min were used.

ANALYTICAL METHOD

Analytic control of the ozonation process covered the following determinations:

- pH value;
- Dichromate COD;
- Permanganate COD (see appendix A);
- BOD_5 by dilution method;
- Spectrophotometric color measurements, determined in a continuous way on a Carl Zeiss Jena UV-VIS Specord apparatus. Light absorption measurements were conducted in the range 360 to 560 nm. The average light absorption value was calculated from 10 points on a curve plotted in equal segments of the spectrum length. In preliminary investigations, when dyes added to water or wastewater were determined, the absorption value was read off at the dominant wavelength;
- Color, Co-Pt scale;
- Color threshold by dilution method;
- Conductivity by conductometric method;
- Turbidity by nephelometric method in a Carl Zeiss Jena turbidimeter;
- Anionic detergents;
- Nonionic detergents by the phospho-tungstic acid method with the hydroquinone modification (see appendix A);
- Total organic carbon with a carbon analyzer (Beckman Model 915A);

- Ozone in the wastewater by the iodometric method [1]; and
- Ozone in the gas by the iodometric method [1].

The values of ozone concentrations in wastewater and in the gas leaving the column after the process formed the basis for calculation of the percentage balance of ozone. The COD indicator was used to calculate the theoretical ozone demand required for the oxidation of dyes added to water and wastewater in the laboratory investigations. COD determinations were performed for the dyes under examination; and these are presented in table 9-1 in relation to 1 mg of dye. On the basis of these values, and known values of the concentration of ozone in the gas, the amount of gas supplied in a unit of time, and the dye concentration, the total amount of ozone supplied and the theoretical time required for the total oxidation of the dye were calculated.

OZONATION CARRIED OUT IN A BATCH SYSTEM ON A LABORATORY SCALE

Ozone Oxidation of Water Solutions of Single Dyes

Equipment and Procedure--

The investigations were carried out on a laboratory scale by means of the model apparatus presented in figure 9-1. The ozone-air mixture was obtained in a Trailigaz ozone generator installed in the waterworks in Cracow. The generator has the following specifications:

- When 60 to 70 m^3 of air/h is introduced to the generator, its capacity rises to 1 kg O_3/h,
- The generator voltage is 14 kV,
- The air pressure at the input of the generator is 0.58 to 0.68 bar, and
- The power is 15 to 17 kW.

The mixture of air and ozone was fed through a fritted glass diffuser into the reaction chamber, along with 750 ml of the solution under examination. The ozone concentration in the feed mixture fed in was 10 to 15 mg/l.

From the reaction vessel, air containing unreacted ozone passed to a trap where the ozone surplus reacted with a solution of potassium iodide. The gas flow was measured in a dry gas meter. Each of the solutions prepared for investigation contained 50 mg/l of a single dye or 50 mg/l of each of two or more dyes.

Before ozonation was carried out, the airtightness of the whole system was checked; after the ozone-air mixture inflow was switched on, the flow and ozone concentration were regulated. Next, the solution under investigation was placed in the reaction vessel shown in figure 9-1, and ozonation was carried out for a definite period of time. For each of the dyes under examination, ozonation of three to four samples was performed, with the ozonation time for each sample longer than for the previous one. Ozonation of the last sample was carried out until all observable color change ceased. The volume of the ozonated sample remained unchanged until the end of the process.

After the ozonation of each sample was completed, the quantity of unreacted ozone in the sample examined and the remaining ozone in the air absorbed in the potassium iodide solution were determined.

Comment on the Results--

The investigations were carried out with single dyes from different functional groups (17 dyes in all, shown in table 9-2). The dyes were fed into tap water to eliminate interference of other substances contained in wastewater.

The percentage of ozone balance calculated in table 9-3 indicates that in the majority of cases the consumption of ozone in the oxidation process does not exceed 50 percent of the total amount of ozone fed into the sample. As the reaction time is prolonged, the consumption of ozone in the majority of cases diminishes owing to the decrease of rate of the oxidation reaction. Correspondingly, when the oxidation reaction time is prolonged, ozone losses increase.

Several of the dyes examined show a color reduction from 70 to 90 percent with an ozone contact time of 20 min or less (table 9-4). These are mostly dyes from the glacial and reactive groups. The presence of single benzene or naphthalene rings in the structure of these dyes activated by oxygen or nitrogen functional groups can explain the greater susceptibility of these compounds to the effect of ozone through the formation of transitional and unstable quinone or imino-quinone groups. A feature of the imino-quinone groups is the particular ease with which their nucleus structures decompose under the influence of ozone. Also the dyes of the sulfuric group (with the exception of Sulphur Brown W4R) readily react with ozone, which splits and oxidizes the polysulfide chains and the thiazine rings, and leads to the degradation of the dye.

The remaining dyes under investigation require prolonged ozonation time. Two of them, Synten Rubine P-3B (C.I. Disperse Red 5; 11215) from the dispersed group and Helanthrene Green from the vat group, with contact times of 20 to 90 min respectively, show color reductions of only 37 percent and 41 percent. The resistance of these dyes to ozonation can be explained by the presence of condensed polycyclic compounds.

Changes of light adsorption in the range of 360 to 650 nm for two characteristic dyes, Salt of Naphthanil Blue and Helanthrene Green, are presented in figures 9-2 and 9-3. Curves of percentage color removal are plotted against oxidation time in figure 9-4. These curves indicate the possibility of achieving total color removal by considerably prolonging oxidation time, even for solutions of dyes resistant to oxidation (with the exception of Sulphur Brown W4R). However, for the sake of economy, a process time longer than 30 min cannot be considered. Determinations of color threshold (table 9-4) confirm the course of the color removal process determined spectrophotometrically.

Oxidation with ozone caused a fall in COD value in the majority of cases (table 9-4). COD reduction after a contact time of 15 to 20 min reached 25 to 40 percent. A higher degree of COD removal--60 to 80 percent--

was achieved after a considerably longer contact time (90 to 120 min). For dyes from the reactive group (Helaktyn Yellow D-5GN and Helaktyn Red F5B) an increase of COD content was found in the first phase of ozonation. COD value diminished only in the later phase of ozonation. For dyes from the sulfuric group, the COD value remained unchanged during ozonation.

Ozone Oxidation of Individual Dyes Fed to Wastewater

Comment on the Results--

The studies were carried out on individual dyes (nine in all, shown in table 9-5) fed into biologically treated wastewater.

Biologically treated wastewater, collected twice for investigations in this series (table 9-6), was characterized by a common yellow-green color. This wastewater showed a different degree of color removal in the ozonation process (from 22.2 percent to 68.9 percent after 40 min and a high percentage of COD removal (53.4 percent after 40 min in one sample).

Removal of anionic detergents amounted to from 45 percent to 65.4 percent after 40 min; removal of nonionic detergents after the same time was from 28.3 percent to 75 percent (table 9-6).

The solutions of most dyes in wastewater submitted to ozonation displayed ozone consumption lower than 50 percent (table 9-7). Only Salt of Naphthanil Blue BT, Helaktyn Red F5B, and Sulphur Black WT (C.I. Solubilised Sulphur Black 1; 53186) displayed ozone consumptions higher than 50 percent of the amount of ozone fed in. In the majority of cases, the ozone consumption diminished as the reaction time was prolonged.

The ozone balance drawn up (table 9-7) shows that the ozone losses ran within the extremes of 36.4 percent for the salt of Naphthanil Blue BT to 90.7 percent in the case of Scarlet Base. The pH reaction of the samples changed very slightly in the course of ozonation (the maximum by 0.55 units). Turbidity also lessened very little.

Measurements carried out during ozonation (table 9-6) show that conductivity after different process duration times was nearly constant.

Of the nine dyes examined, three show a considerable decrease in color from 70 to 93 percent with a 40 min or less contact time (table 9-6). It was found that the dyes Synten Rubine P-3B (C.I. Disperse Red 5; 11215) and Helanthrene Green B5, which decolorize very slightly in a tap water solution, are also resistant to oxidation in a wastewater medium. They decolorized, respectively, by 57.3 percent after 90 min, and by 9.7 percent after 120 min of oxidation (table 9-6). The dyes Sulphur Brown W4R and Helasol Green ZG are also subject to slight color removal--the first to 11 percent after 20 min, the second to 28 percent after 96 min.

The curves of percentage color removal are plotted against oxidation time in figure 9-5. These curves indicate that by considerably prolonging oxidation time, total color removal can probably be achieved for all the dyes under investigation with the exception of Sulphur Brown W4R. In both the first and second series of investigations, this dye behaves in a similar way during ozonation, achieving a certain maximum of decolorization, after which the percentage of color removal diminishes again (figures 9-4 and 9-5). Color threshold values remain closely dependent on the percentage of color removal determined spectrophotometrically (table 9-6). Most ozonated dye solutions showed a consistent reduction of COD content (table 9-6), achieving a 16 to 71 percent reduction after 20- to 120-min contact time.

For dyes from the reactive and sulfuric groups, analogous to the first series of investigations, COD value first increased and later decreased (table 9-6).

The organic carbon content in the biologically treated wastewater was 16 to 18 mg/l. After individual dyes were introduced to the wastewater, the organic carbon content occasionally grew considerably--for a solution of Sulphur Black WT (C.I. Solubilised Sulphur Black 1; 53186), to 27.5 mg/l. The percentage removal of organic carbon in the ozone oxidation process was very inconsistent, and, after the longest contact time in wastewater without dyes added, amounted to 47 percent.

The highest degree of organic carbon removal occurred for Helaktyn Yellow (83.7 percent) and the lowest for Helanthrene Green (16.7 percent). In the remaining dye solutions, percentage removal varied from 40 to 74 percent. The degree of organic carbon removal roughly coincided with the degree of color removal.

Ozone Oxidation of Dye Mixtures Introduced to Wastewater

Comment on the Results--

Investigations were carried out for the following five kinds of mixtures of two or three dyes*:

Mixture No. 1:	Salt of Naphthanil Blue BT (Glacial) Helanthrene Green B5 (vat)
Mixture No. 2:	Sulphur Black WT (sulfuric) Scarlet Base RG (glacial) Helaktyn Red F5B (reactive)
Mixture No. 3:	Helasol Green 2G (indigosol) Helaktyn Yellow DGR (reactive) Indanthren Bordeaux RR (dispersed)
Mixture No. 4:	Synten Azure (dispersed) Helasol Yellow GOK (indigosol) Drimarene Green X-2BL (reactive)
Mixture No. 5:	Helaktyn Yellow D-5GN (reactive) Helasol Grey BL (indigosol)

The dyes constituting the mixtures differed in color. The concentration of individual dyes was 50 mg/l. In the ozonation process, solutions of all the dye mixtures showed ozone consumption greater than 50 percent of the amount of ozone supplied (table 9-7). The concentration of ozone in the ozone-air mixture fed in, similar to that in the oxidation process of individual dyes, amounted to 10 to 12 mg/l.

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*See pages 12 and 13 for Colour Index information on each of these dyes.

The ozone balance drawn up (table 9-7) shows that ozone losses in the oxidation process ranged from 5.3 percent for mixture 2 to 56.3 percent for mixture 3. When the mixtures were being oxidized the maximum change in pH was 0.45 units (table 9-6).

Color removal for mixtures of dyes is considerably slower than for single dyes, on account of the higher concentrations of dyes in the mixtures and the use of mixtures of dyes from different functional groups that undergo decolorization to a varying degree. A 38 to 91 percent reduction of coloring was achieved only after 50 to 180 min had elapsed (table 9-6).

Mixture 1, composed of Helanthrene Green, which is difficult to remove, de-colorized by 38.4 percent only after 180 min of ozonation. The curves of percentage color removal plotted against contact time, presented in figure 9-6, indicate that for mixtures 2 and 5, when an ozone concentration of about 10 mg/l is used, full color removal can probably be achieved in 110 to 130 min. But for mixtures 1, 3, and 4, it would be possible to achieve full color removal only with a very long ozone contact time.

The contact time required for decolorization of the mixtures of dyes was in each case greater than the sum of time necessary for decolorization of individual dyes contained in the mixture.

The COD decreased as ozonation took place, and with contact times of 60 to 180 min, COD was reduced as much as 30 to 40 percent. Removal of organic carbon was relatively small--from 18.8 to 29 percent after the longest contact time.

Ozone Oxidation of Dyes Having Different Concentrations

Comment on the Results--

The investigations were carried out for three individual dyes introduced to biologically treated wastewater: Scarlet Base RG, Salt of Naphthanil Blue BT, and Helaktyn Yellow D-5GN. Dyes were chosen that are quite easily removed under the influence of ozone. The concentrations of dyes totaled 50, 75, and 100 mg/l. The amount of ozone introduced was also held constant at 32.6 mg. A constant ozone-wastewater contact time of 25 min was used (table 9-8). A control test was conducted by submitting biologically treated wastewater to ozonation without the addition of dyes.

The following analytical determinations were performed: color measured spectrophotometrically, color threshold, and dichromate COD. The percentage of color removal according to dye concentration is given in table 9-9 and graphically displayed in figure 9-7. It is clear from these studies that with the increase of dye concentration the degree of color removal decreases by 19 to 25 points. But the degree of COD removal is irregular; at the highest dye concentration applied it equals 100 mg/l, varying from 21 to 25 percent (table 9-9).

The technical parameters of the oxidation process and the ozone balance are summarized in table 9-8. The ozone balance indicates that the amount of ozone consumed by the sample under investigation grows by 9 to 28 percent as the concentration increases (figure 9-8).

Discussion of Results of Batch Laboratory Investigations

The consumption of ozone by the samples studied in these investigations usually did not reach 50 percent of the total amount of ozone introduced. Consequently, ozone losses were considerable, whereas in other research [59], on removal of COD and TOC from wastewater, ozone losses reached a maximum of 40 percent. This results from the conditions under which the process is conducted in the model reaction chamber, in which hydrodynamic conditions deviate from the operational scale.

To decrease ozone losses, it is necessary to apply a reaction chamber with the contact surface of oxidized wastewater and ozone-air mixture increased to the maximum. It was found in the investigations that the percentage of consumed ozone is higher when dyes are oxidized in wastewater media [55] than in tap water. The ozone consumption was also higher for dye mixtures with the highest concentration of substances introduced.

The ozone balance data given in tables 9-3 and 9-7 show that a high percentage of the ozone introduced to the sample appeared in the exit gas. Increasing the height of the reaction vessel, and consequently the reaction time between the zone and the sample, might have reduced this ozone loss.

The decrease of turbidity found in previous research [58] was not confirmed in the present research, probably on account of the very slight initial turbidity of the wastewater. Nor was there found any decomposition of the mineral salts contained in wastewater under the influence of ozonation.

The highest percentages of color removal appeared in solutions of single dyes in tap water (37 to 98.8 percent). Somewhat lower values (11 to 97 percent) were obtained for dyes dissolved in wastewater, and the lowest degree of color removal (38 to 91 percent) was obtained during oxidation of dye mixtures with the highest dye concentration. Dyes from the glacial, dispersed, reactive, and indigosol groups decolored to a considerable degree, dyes of the vat and sulfuric groups to a lesser degree.

The range of COD removal from 30 to 40 percent obtained for the dye mixtures 1 to 5 with a contact time of 60 to 180 min is consistent with data in the literature [54,55,57,58,59]. It seems that a higher percentage of COD removal, from 50 to 70 percent, can be obtained, as past [54] and present research show, by prolonging the contact time of wastewater and ozone. This would be uneconomical, however.

For dyes of the reactive and sulfuric groups, an initial increase in COD was found, followed by a reduction as ozonation progressed. One of the most probable reasons for this phenomenon is ozone's capacity of acting on and splitting organic compounds present in wastewater and transforming them into compounds more susceptible to the COD test [62].

The percentage of organic carbon removal in the ozone oxidation process was very inconsistent. After the longest reaction time applied, for wastewater without the addition of dyes it was at least 36 percent, and for single dye solutions it was 16.7 to 83 percent.

A low degree of organic carbon removal was obtained in dye mixtures. The relation between organic carbon and COD shows a fairly considerable dispersion (figure 9-9). A greater dispersion occurred in wastewater which was not submitted to ozonation. In ozonated wastewater, the scatter was somewhat less.

Investigations showed that the ozonation process is useful for removing anionic detergents (45 to 65 percent reduction) and nonionic detergents (28 to 75 percent reduction).

OZONATION OF BIOLOGICALLY TREATED WASTEWATER IN A CONTINUOUS SYSTEM

Cocurrent Ozonation on a Laboratory Scale

Equipment and Procedure--

Investigations were carried out in a glass column 145 cm high and 5.4 cm in diameter (figure 9-10). The column was filled to a height of 135 cm with ceramic Raschig rings, which insured uniform distribution of gas in the column. The ozone was generated from oxygen in a Fischer generator (Model 503) with the following specifications: minimum ozone capacity--2 g/h with Q = 50 l of O_2/h, and maximum ozone capacity--16 g/h with Q = 500 l of O_2/h. When ozone concentrations lower than the generator capacity allowed for were required, oxygen was added to the ozone-air mixture generated by the generator. The ozonation process was carried out cocurrently with feeding of the ozone-oxygen mixture through a diffuser and the wastewater through a rotameter, both at the bottom of the column. The working capacity of the column was 2 l. A diagram of the equipment is given in figure 9-10.

Biologically treated and filtered wastewater from the experimental station in Andrychow was used for the investigations. Before each test, the column was stabilized to constant conditions by letting an ozone-oxygen mixture pass through it for about 2 h. Next, the ozone concentration required was accurately controlled and the wastewater was fed in.

Seven tests were carried out, lasting from 80 to 240 min. Three different ozone doses were used, which, with reference to wastewater, gave the concentrations: 55.0, 77.7, and 134.7 mg/l. A wastewater detention time varying from 10 to 32 min was used. During each test, samples of wastewater flowing into and out of the column were collected four or five times at equal intervals. At the same time, samples were collected for determination of the content of ozone fed to the column, ozone in the wastewater after the process, and ozone in the gas leaving the column.

Comment on the Results--

On the basis of the seven tests carried out, the ozone dose and contact time required in the oxidation process with continuous wastewater flow were determined. The wastewater was collected for the research on two different days, and its chemical composition fairly differentiated. The COD content was 146 and 226 mg/l. The anionic detergent content was 0.50 and 1.40 mg/l, and the nonionic detergent content was 8.3 and 15.3 mg/l. The color of the wastewater was intensely pink. The pH was 8.0 and 8.3 (table 9-10). The percentage ozone balance (table 9-10) shows that the degree of ozone consumption is not proportional to the contact time and the amount of ozone fed in. In tests 2, 3, 4, and 7, with the same ozone concentration of 55 mg/l and approximate detention time of 21 to 32 min, differences arising in the ozone balance were large--for the ozone consumed in the process they amounted on the average to: for test No. 2--55.2 percent; for test No. 3--48.5 percent; for test No. 4--62.3 percent; and for test No. 7--70.3 percent. In tests 5 and 6 with different ozone concentrations (134 and 77 mg/l), the degree of consumed ozone was respectively 65 and 50 percent. The average degree of pollutant removal also showed great divergence in results under the same process conditions. The degree of pollutant removal obtained was: for color, from 29.1 to 62 percent; for COD, from 10.9 to 41.6 percent; for anionic detergents, from 26.3 to 80 percent; for nonionic detergents, from 28.8 to 73.9 percent. The pH fell slightly.

The results are presented in table 9-10. The ozonation system used did not give a definite answer as to the optimum conditions for carrying out the process on a larger scale.

One-State Ozonation on the Pilot Scale

Equipment and Procedure--

The research was carried out at the experimental station in Andrychow on wastewater that had been biologically treated and then filtered through a sand bed. The equipment consisted of a Plexiglas column 2 m high and 12 cm in diameter. The column was filled to the height of 1.5 m with ceramic Raschig rings. The column operated countercurrently, according to the scheme presented in figure 9-11. The ozone was generated from oxygen in a Fischer Labor generator. The ozone-oxygen mixture was fed to the column through a rotameter and porous glass diffuser that filled the whole bottom of the column.

Before each test, the column was stabilized to constant conditions for about 2 h. After this, the ozone concentration required was regulated and the wastewater was fed in. Forty-four tests (tests 8 to 51) were carried out. A test lasted, on the average, 6 h. The ozone concentration in individual tests was changed within the range of 10, 30, 50, or 70 mg/l of wastewater. The wastewater was retained in the column for 15, 30, 40, and 50 min. The amount of ozone fed in ranged from 0.5 g/h to 1.7 g/h with a wastewater flow from 19.2 l/h to 48 l/h, according to the concentration required. The ozone balance completed for 44 tests (table 9-11) shows that the amount of ozone consumed and decomposed in the column varies from 61 to 66 percent of the total amount fed in. Only in tests 13 to 18 did increased ozone consumption--from 76 to 81 percent--occur.

Comment on the Results--

The wastewater fed into the column varied in chemical composition. Its color was intensely pink, except in tests 43 to 48, when it was grey-green. The average color value, which was measured spectrophotometrically as extinction, was 0.134 to 0.450. Wastewater pH varied from 6.8 to 8.0, but it was mainly 7.5 or 7.7. Dichromate COD varied from 69.1 to 201.2 mg/l, permanganate COD from 14.4 to 52.8 mg/l, anionic detergents from 0.33 to 1.14 mg/l, and nonionic detergents from 4.6 to 28.7 mg/l. During ozonation the wastewater color changed to yellow-green, comparable with the Pt-Co scale. The pollutant removal effects were higher the greater the ozone dose used (tables 9-11 and 9-12).

With a sample ozone concentration of about 10 mg/l, according to the contact time, color removal was from 5.0 to 32 percent, permanganate COD removal from 5.5 to 16.2 percent, dichromate COD removal from 0.0 percent (with a contact time of 15 min) to 17.0 percent, anionic detergent removal from 16 to 36.8 percent, and nonionic detergent removal from 5.4 to 30.3 percent.

With an ozone concentration of about 30 mg/l, the color removal was from 9.9 to 50.4 percent, permanganate COD removal from 6.6 to 24.5 percent, dichromate COD removal from 1.8 to 28 percent, anionic detergent removal from 31 to 54.4 percent, and nonionic detergent removal from 13.6 to 46.4 percent.

With an ozone concentration of about 50 mg/l, color removal was from 17.4 to 52.9 percent, permanganate COD removal from 6.2 to 34.8 percent, dichromate COD removal from 2.7 to 31.6 percent, anionic detergent removal from 42.5 to 70.1 percent, and nonionic detergent removal from 24.7 to 55.6 percent.

With an ozone concentration of about 70 mg/l, color removal was from 39.7 to 56.6 percent, permanganate COD removal from 14.9 to 32 percent, dichromate COD removal from 10 to 33.6 percent, anionic detergent removal from 67.3 to 89.4 percent, and nonionic detergent removal from 37 to 63.7 percent.

Irrespective of the ozone concentration, permanganate COD decreased fairly irregularly to a maximum of 34.8 percent, BOD_5 was removed up to 25 percent. In 16 tests the BOD_5 concentration did not change. The present investigations showed that the optimum range of time in which the best effects were obtained irrespective of ozone dose used was 30 to 40 min. Above this time the degree of removal of individual pollutants clearly diminishes (figure 9-12).

Double-Stage Ozonation on the Pilot Scale

Equipment and Procedure--

The investigations were carried out at the experimental station in Andrychow. The equipment consisted of two Plexiglas columns, each 2 m high and 12 cm in diameter. The columns were filled to a height of 1.5 m with ceramic Raschig rings (figure 9-13). The first column operated countercurrently, the second cocurrently. The wastewater was fed into the first column from above, and the ozone-oxygen mixture was fed in at the bottom through a rotameter and diffuser. After passing through the first column, the wastewater, together with a new dose of ozone, was directed from the bottom to the second column.

The ozone was generated in a Fisher Labor generator. Research on double-stage ozonation included 24 tests (tests 52 to 75). Four different ozone concentrations, of about 10, 30, 50, and 70 mg/l, were used. Both the ozone concentrations and detention times are given together for the set of two columns. Each column accounted for exactly half the detention time, and half the ozone concentration was applied to each. The amount of ozone fed in was from 0.5 g/h to 9.5 g/h, with a wastewater flow from 38.4 to 128 l/h, depending on the concentration required. The individual tests lasted on the average 6 h. After ozonation, samples of wastewater at inflow and at outflow were collected from the second column several times during the course of the test and were poured into an average sample intended for analysis.

Measurements of ozone in the gas fed in and in the gas discharged from the first and second column were performed several times during each test. The amount of ozone in the wastewater after ozonation was determined entirely at the outflow from the second column. The percentage ozone balance was calculated using average values.

Comment on the Results--

The ozone balance completed for 24 tests (table 9-13) shows that the amount of ozone consumed and decomposed in the two columns varies within the range of 52 to 63 percent. Only in tests 60 and 61 was the ozone consumption higher, totaling 68 and 71 percent.

The unreacted ozone in the exhaust gas was from 22 to 45 percent. Additional determinations of ozone in the exhaust gas performed during the course of tests show that the utilization of ozone in the reaction with organic compounds was higher in the first column. This is evidenced by the amount of ozone in the gas, which was 25 percent lower than the ozone in the gas after the second column.

Wastewater fed to the set during tests 52 to 75 varied in chemical composition (tables 9-13 and 9-14). The wastewater color was intensely pink or grey-green. The average absorption value from the spectrophotometric measurement of color was from 0.281 to 0.436; the wastewater pH was from 7.2 to 8.0. Dichromate COD removal was from 91.5 to 289 mg/l; permanganate COD removal was from 22.0 to 84.6 mg/l; anionic detergent removal was from 0.35 to 0.89 mg/l; and nonionic detergent removal was from 6.75 to 31.6 mg/l. The pollutant removal depended on the ozone concentration, but not on the detention time as in the one-stage system. Because the ozone losses caused by its decomposition were made up, the ozone concentraton did not diminish with a longer reaction time. Thus, pollutant reductions were higher (figure 9-14).

Pollutant removal with an ozone dose of about 10 mg/l in individual series ranged from 45.8 to 47 percent for color, from 10.0 to 18.8 percent for dichromate COD, from 49.6 to 51.0 percent for anionic detergents, and from 25.7 to 44.6 percent for nonionic detergents (table 9-15).

With an ozone dose of about 30 mg/l, color removal ranged from 54.1 to 56.5 percent, dichromate COD removal from 12.9 to 17.8 percent, anionic detergent removal from 68.4 to 69.6 percent, and nonionic detergent removal from 35.4 to 51.7 percent.

With an ozone dose of about 50 mg/l, color removal ranged from 59.5 to 60.1 percent, dichromate COD removal from 20.0 to 21.3 percent, anionic detergent removal from 82.7 to 84.9 percent, and nonionic detergent removal from 43 to 60 percent.

With an ozone dose about 70 mg/l, color removal was from 64.4 to 67.3 percent, dichromate COD removal from 26.4 to 27.2 percent, anionic detergent removal from 85.3 to 86.9 percent, and nonionic detergent removal from 53.1 to 60.8 percent.

Wastewater pH was subject to only slight variations during ozonation. BOD_5 was subject to slight reduction or remained unchanged (table 9-14).

One-Stage Ozonation of Wastewater After Coagulation and Adsorption on Activated Carbon

Equipment and Procedure--

The process of ozonation was carried out at the experimental station in Andrychow on the one-stage installation (figure 9-11). The research was carried out on wastewater that had been biologically treated and submitted successively to coagulation, filtration, and adsorption on activated carbon.

Before every test the column was stabilized to constant conditions for about 2 h, after which wastewater was fed in; 12 tests (tests 76 to 87) were conducted. Each test lasted 6 to 8 h. The contact time of wastewater with ozone was constant at 30 min. The ozone concentration in tests 76 to 81 was 10 mg/l of wastewater; in tests 82 to 87, it was 5 mg/l of wastewater. The amount of ozone in the gas was from 0.16 g/h to 0.32 g/h, with a constant wastewater flow of 32 l/h.

During the course of each test, wastewater samples were collected several times from the inflow and outflow of the column and were poured together into one average sample intended for analysis. Measurements were also made of ozone in the gas fed into and leaving the column and in wastewater after ozonation.

Comment on the Results--

The ozone balance made for 12 tests (table 9-16) shows that the amount of ozone fed into the wastewater in a concentration of 10 mg/l was too high. As a result, the amount of unreacted ozone in the wastewater was high: from 17 to 35 percent of the ozone fed in. The amount of ozone in the gas after the process was also high--from 37 to 41 percent. The amount of ozone consumed ranged from 25 to 44 percent.

When the concentration of ozone fed in was decreased by a half to 50 mg/l, consumption remained practically unchanged. The amount of unreacted ozone in the gas was from 46 to 52 percent, in wastewater from 8 to 16 percent.

The wastewater fed to the column (tables 9-16 and 9-17) after coagulation and adsorption on carbon was very pure. The pH ranged from 6.9 to 8.0. Color was very low--on the Pt-Co scale from 5 to 15 mg/l. BOD_5 concentration varied from 1.5 to 3.2 mg/l, dichromate COD from 1.5 to 14.3 mg/l, permanganate COD from 0.3 to 2.3 mg/l, total organic carbon (TOC) from 2.5 to 7.3 mg/l, and nonionic detergents from 2.0 to 4.75 mg/l. No anionic detergents were found, or they appeared only in trace amounts. Wastewater pH after ozonation remained unchanged. The BOD_5 residual was up to 2.9 mg/l after ozonation. A reduction of BOD_5 by a maximum of 61 percent was found. In five tests no reduction was noted.

Removal of dichromate and permanganate COD was from 0 to 66.6 percent, in proportion to the concentration in the inflow. The concentration of total organic carbon was low--up to 6.7 mg/l.

The removal of carbon during ozonation was very slight, and in four tests a slight increase of value was noted. Nonionic detergents showed the highest decrease during ozonation--from 15.8 to 46.2 percent. The final concentration of detergents was from 1.25 to 4.0 mg/l.

Discussion of Results of Studies in a Continuous System

The investigations were carried out on a pilot scale in a one-stage and in a double-stage system. Four different ozone concentrations of about 10, 30, 50, and 70 mg/l of wastewater, and different contact times of 15, 30, 40, and 50 min were applied.

It is clear from the ozone balance that the one-stage ozonation process was carried out with an ozone deficit. This is indicated by the small concentrations of ozone still in the wastewater after the process.

The double-stage ozonation process was carried out with an ozone surplus, particularly in the second stage. The course of the oxidation process and the degree of pollutant removal was differentiated according to the system used. The relation between removal in percentages of such pollutants as color, COD, anionic and nonionic detergents, and reaction time with four different ozone doses used--about 10, 30, 50, and 70 mg/l--is presented graphically in figures 9-12 and 9-14.

The basic difference in the results of the one- and two-stage systems is that the one-stage ozonation system required a longer wastewater-ozone contact time to obtain optimal pollutant removal. This was from 30 to 40 min, depending on the type of pollutant. Prolonging or shortening the ozonation time reduced treatment effectiveness (figure 9-12). When the ozonation time was prolonged to 50 min, there was a clear decrease in the removal of all pollutants as a result of the decomposition of the ozone prior to reaction with pollutants.

When double-stage ozone dosing was applied, pollutant removal occurred considerably more quickly. After the process had been carried out for 15 min, the maximum degree of pollutant removal, which practically did not change in time (figure 9-14), was achieved. No reduction in level of pollutant removal was found when the contact time was prolonged to 50 min while maintaining a constant ozone concentration.

The results of color removal obtained (maximum 67 percent) are somewhat lower than those quoted in the literature [54,62,63,64,65,66]. For example, for concentrated textile wastewater, up to 80 percent of color removal was obtained, while for municipal biologically treated wastewater, up to 92 percent was obtained.

In the research under discussion, the dichromate COD was removed to a maximum of 31 percent, to a degree consistent with data in the literature [54,62,63,64,65,66]. The growth in COD value in wastewater after ozonation was not observed as it was in the present studies when dye solutions were oxidized.

Increase in COD value is discussed in the literature [62,63,64]. This phenomenon occurs as a result of the decomposition in wastewater of large aromatic compounds such as dyes under the action of ozone. Ozone attacks double bonds preferentially.

The large aromatic compounds could be broken into smaller organics, which could then be oxidized more easily by the COD test. For this reason, any comparison of COD value of wastewater before and after ozonation and interpretation of the results obtained should be treated with great care. In a single stage system, BOD_5 was removed to a maximum of 25 percent, and in a double-stage system, to a maximum of 28.8 percent. In many tests it remained unchanged regardless of ozone concentration and retention time. The initial BOD_5 value did not affect the degree of removal.

An instance analogous to the nonremoval of BOD_5 in biologically treated and ozonated wastewater is quoted in the literature [65].

Data on the removal of detergents from wastewater by ozone oxidation are scant [54] and refer exclusively to anionic detergents. The degree of removal of anionic detergents obtained in the present research, 86 percent maximum, is consistent with data in the literature. Nonionic detergents in the wastewater were removed to a lesser degree--to a maximum of 60 percent.

A comparison of the average values of percentage pollutant removal obtained by the method of single- and double-stage ozonation is given in table 9-15.

All the investigations discussed above concern ozonation of exclusively biologically treated wastewater, with fairly considerable concentrations of particular pollutants. The final stage of these investigations was to check the suitability of using ozone as the last stage in a cycle of processes composed of biological treatment, coagulation, filtration, and adsorption on activated carbon. The ozonation can be carried out either before or after the carbon adsorption.

The decision to perform ozonation after carbon adsorption for this study is supported by the fact that wastewater from the textile industry contains considerable amounts of organic compounds and dyes. These compounds appear mainly in high molecular weight compounds, which are readily adsorbed onto the carbon surface. When the ozonation is provided first, these compounds, under the influence of ozone oxidation, are transformed into compounds with smaller molecules that are adsorbed less readily on activated carbon [62]. Another supporting factor is that the strong action of ozone can have a harmful effect on the carbon structure.

The use of the ozonation process together with coagulation, filtration, and adsorption, was found to be effective exclusively for nonionic detergents. Their degree of removal, which reached 46 percent, was consistent in all the tests carried out. The remaining pollutants such as color, dichromate and permanganate COD, BOD_5, and TOC appeared in the inflow of wastewater after the adsorption process in very small concentrations and underwent ozone oxidation to a very small degree.

The results obtained for wastewater treatment by adsorption on carbon followed by ozonation approximate those quoted in the literature [67].

CONCLUSIONS

1. From preliminary laboratory investigations carried out in a batch system on the susceptibility of 10 or so dyes to oxidation with ozone, it was found that when an 11- to 20-mg of O_3/l of wastewater concentration is applied, color of individual dyes from the glacial, suspended, reactive, and indigosol groups is removed to a considerable degree (from 70 to 90 percent) and in a short time (from 5 to 40 min). Dyes from the sulfuric and vat groups were subject to color reduction to a lesser degree--the former to 70 percent and the latter to 20 percent--and with a longer contact time.

2. When dyes from the reactive and sulfuric groups were oxidized, an increase in COD value was found early in the process. This was subject to reduction only as the extinction continued.

3. The optimum reaction time in the one-stage oxidation system was 30 to 40 min. The optimum ozone concentration for removal of color and dichromate and permanganate COD was 50 mg of O_3 of wastewater. Increasing the ozone concentration did not significantly improve the results. The ozone dose required for removal of anionic and nonionic detergents was 70 mg of O_3/l of wastewater.

4. The removal of color and other pollutants in the wastewater in the one-stage oxidation system was the function of the reaction time and ozone concentration. Prolonging the reaction time beyond 40 min, irrespective of the ozone concentrations applied (10, 30, 50, and 70 mg/l), did not increase the effectiveness of the wastewater treatment.

5. When two-stage oxidation was used, pollutants were removed more quickly. The optimum total reaction time was 15 min.

6. When ozone doses of 10, 30, 50, and 70 mg of O_3/l of wastewater were applied, it was found that two-stage oxidation gives better results than one-stage oxidation, especially for color removal (an additional 12 percent) and anionic detergent removal (9 percent). The remaining pollutant indicators did not show any differences in removal in the one- and two-stage process.

7. Increasing the degree of removal of pollutants from the wastewater caused an increase in ozone demand, and, consequently, in the degree of its utilization. In the conditions in which the experiments were conducted, utilization was relatively low, reaching 65 percent of the total amount of ozone supplied.

8. In the ozone oxidation process, the degree of color removal reached 67 percent, dichromate COD removal 32 percent, and permanganate COD removal 35 percent. BOD_5 was removed up to a maximum of 25 percent and in many of the tests carried out it remained unchanged. The wastewater pH and ammonium nitrogen content remained unchanged.

9. Ozone oxidation was used for wastewater which had previously undergone treatment by activated sludge, filtration, and carbon adsorption. Oxidation had no distinct effects, except for nonionic detergents, which showed 46 percent removal. Other pollutants, such as dichromate and permanganate COD, BOD_5, and total organic carbon, which appear in small concentrations after adsorption, were no longer susceptible to oxidation. The removal of these compounds was slight and occurred irregularly.

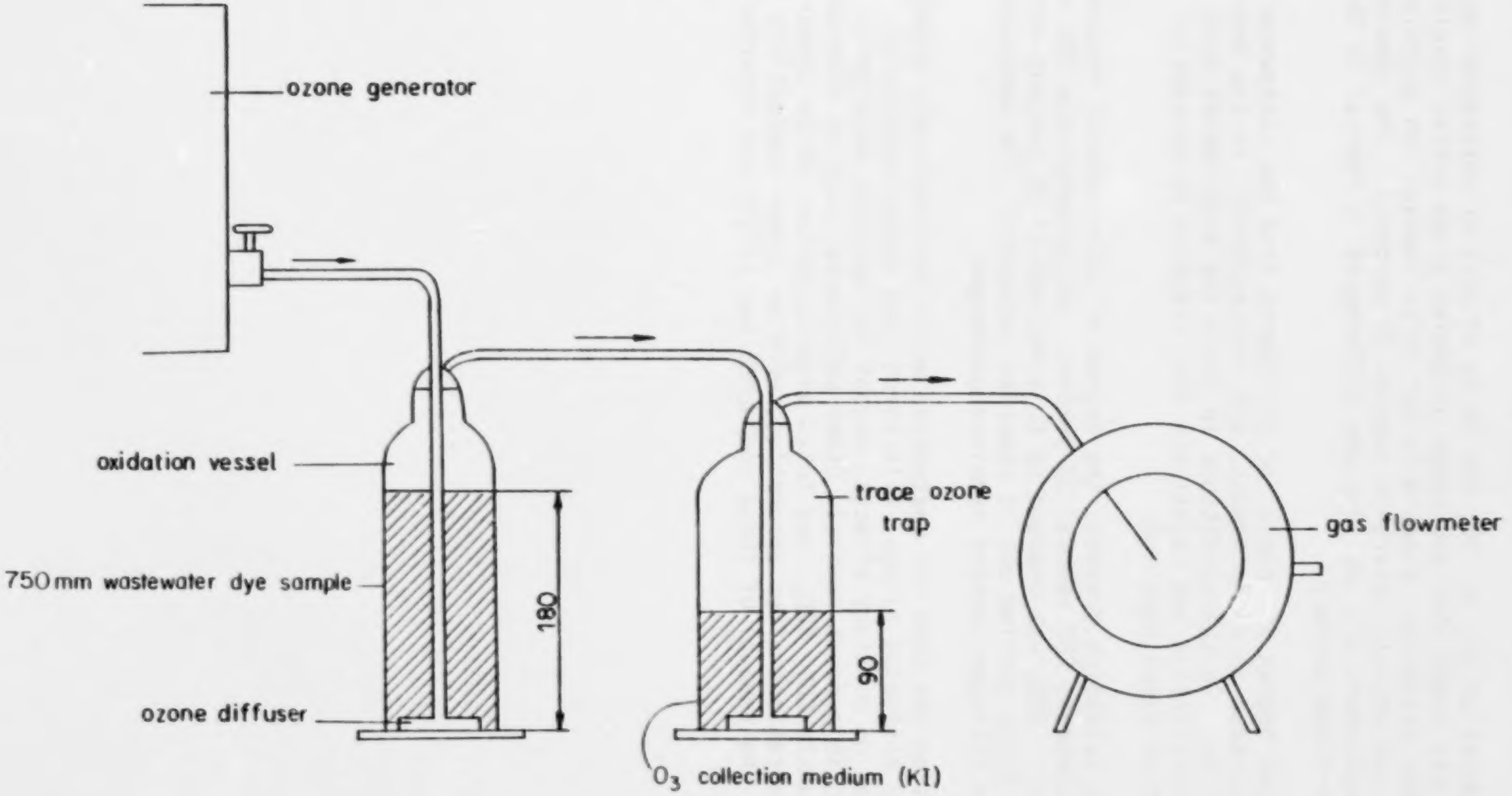

ozone generator
oxidation vessel
750mm wastewater dye sample
ozone diffuser
180
trace ozone trap
90
O_3 collection medium (KI)
gas flowmeter

Figure 9-1. Scheme of ozonation apparatus on a laboratory scale, batch system.

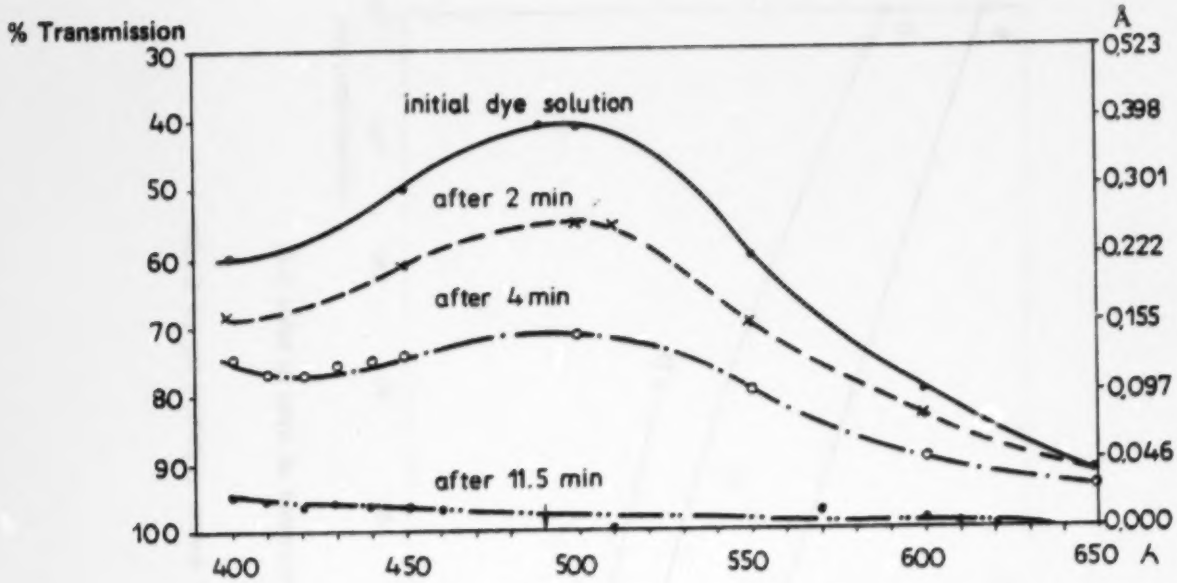


Figure 9-2. Change of absorption spectrum within the λ value. Range from 400 nm to 650 nm for the salt of naphthanil blue BT dye in tap water solution in the course of ozone oxidation process. Ozone concentration in air = 12.7 mg/l, air flow = 18.6 l/h.

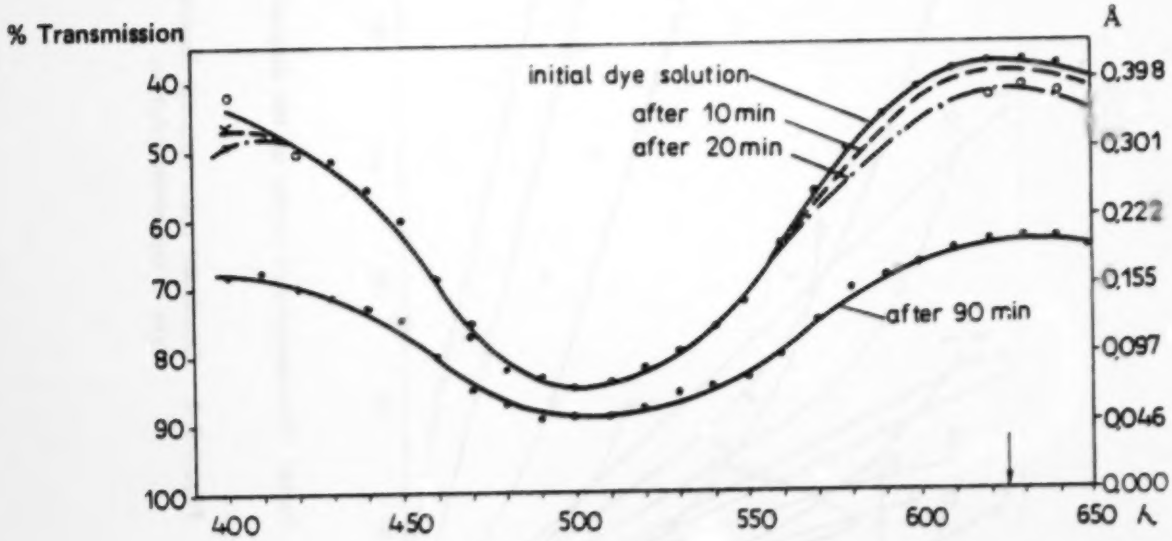
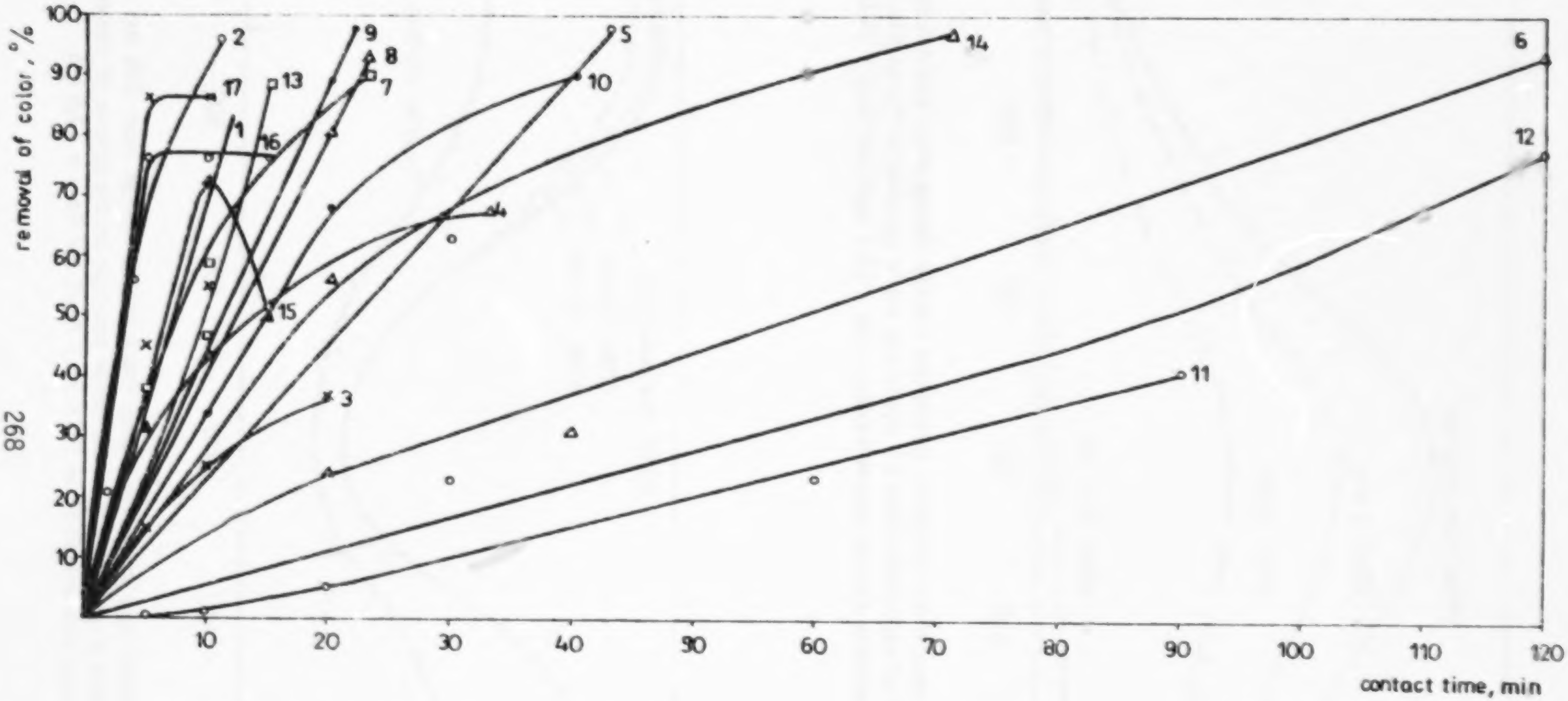
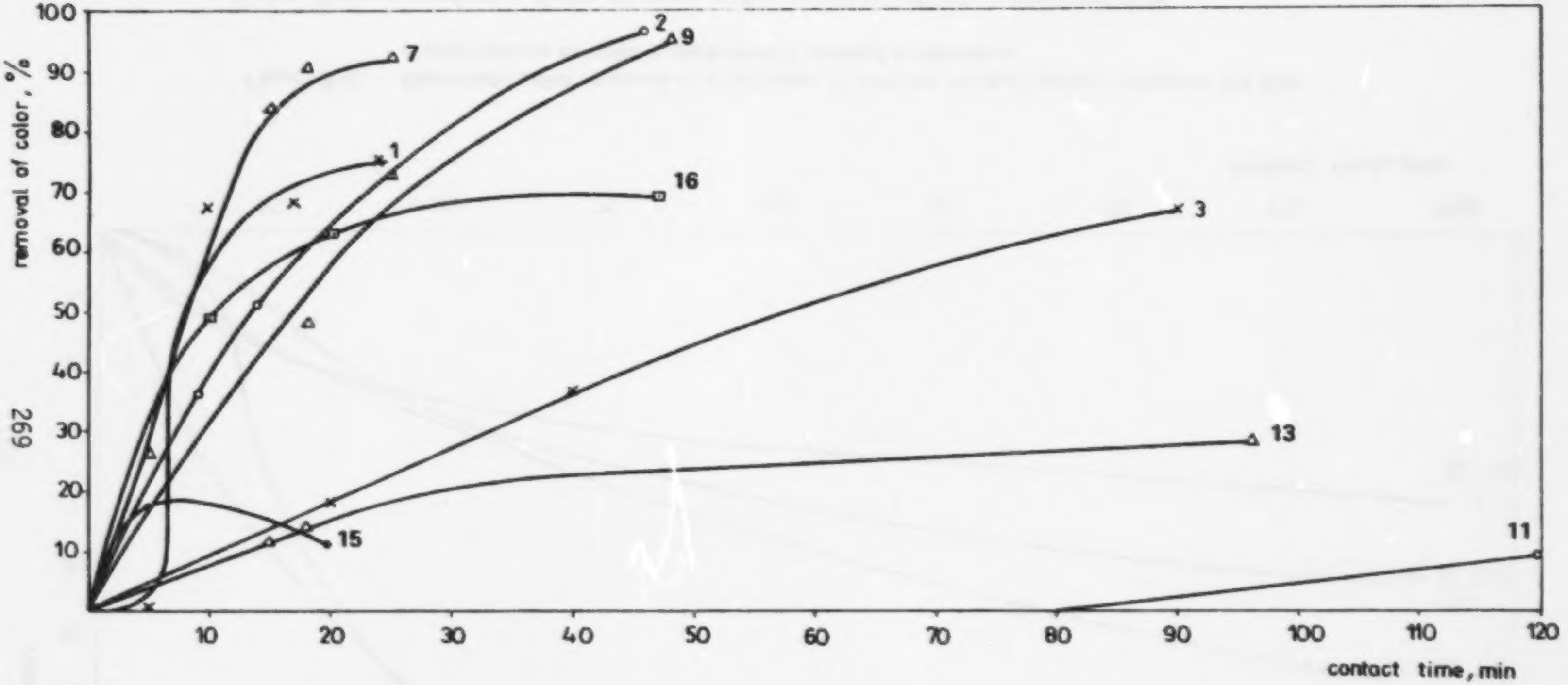


Figure 9-3. Change of absorption spectrum within the λ value. Range from 400 nm to 650 nm for helanthrene green BS dye in tap water solution in the course of ozone oxidation process. Ozone concentration in air = 12.7 mg/l, air flow = 13.5 l/h.



Note: The numbers of curves on the diagram correspond to the numeration of dyes in table 9-5.

Figure 9-4. Dominant color removal depending on contact time of ozone oxidation for particular dyes in tap water solution.



Note: The numbers of curves on the diagram correspond to the numeration of dyes in table 9-2.

Figure 9-5. Dominant color removal as a function of contact time of ozone oxidation for particular dyes in biologically treated wastewater.

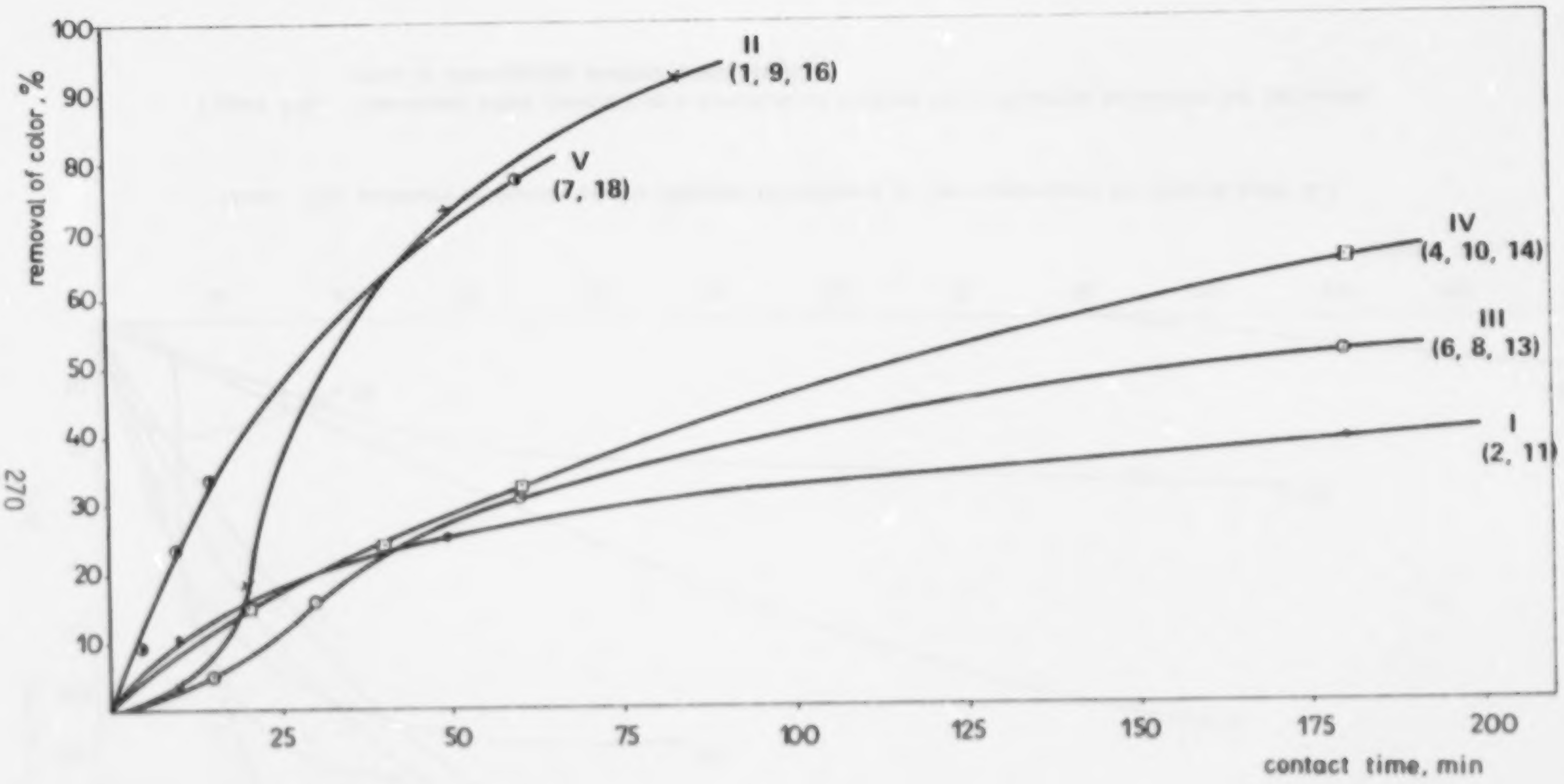


Figure 9-6. Dominant color removal as a function of contact time of ozone oxidation for five combinations of dyes in biologically treated wastewater.

Note: Roman numbers indicate mixture; arabic numbers indicate component dyes.

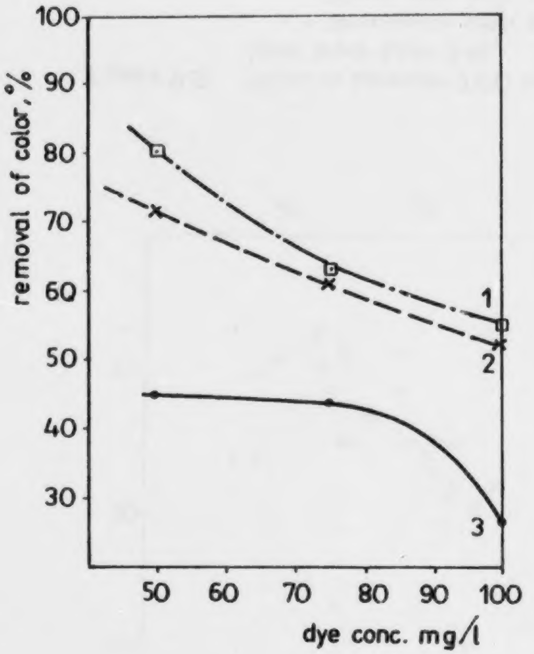


Figure 9-7. Dominant color removal depending on dye concentration for particular dyes in biologically treated wastewater.

1 = the Salt of Naphthanil Blue BT
2 = Helaktyne Yellow D-5 GN
3 = Scarlet Base RG

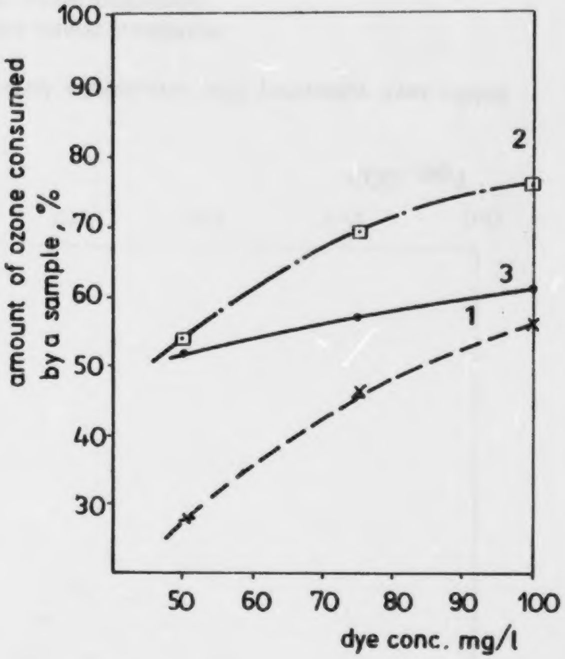


Figure 9-8. Amount of ozone consumed by a sample, depending on dye concentration for particular dyes in biologically treated wastewater.

1 = the Salt of Naphthanil Blue BT
2 = Helaktyne Yellow D-5 GN
3 = Scarlet Base RG

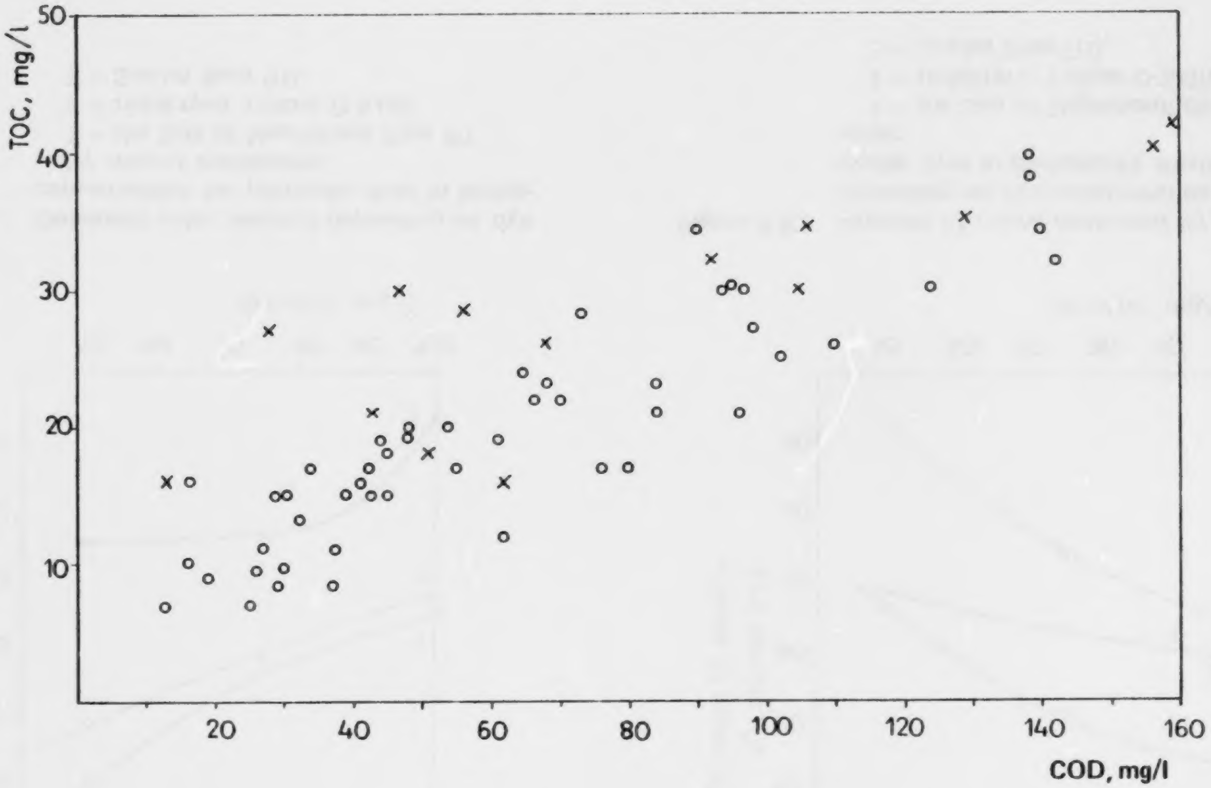


Figure 9-9. Relation between TOC and COD in ozone-treated wastewater with particular dyes added (data from table 9-6).
x = Wastewater with addition of dyes before ozone oxidation
o = Wastewater with addition of dyes after ozone oxidation

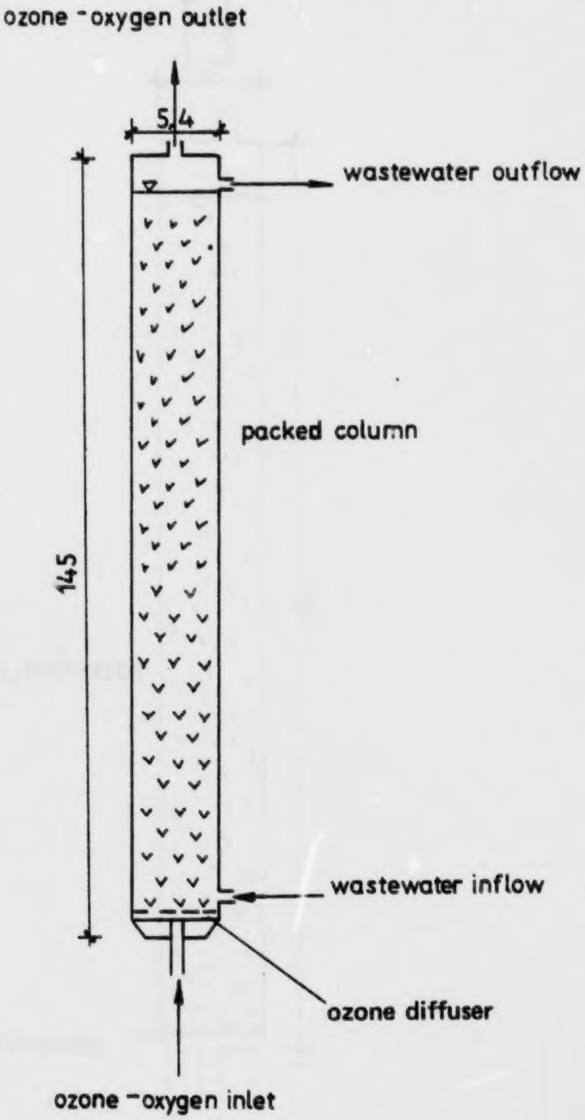

ozone -oxygen outlet
5,4
wastewater outflow
packed column
145
wastewater inflow
ozone diffuser
ozone -oxygen inlet

Figure 9-10. Schematic flow diagram of cocurrent ozonation on a laboratory scale.

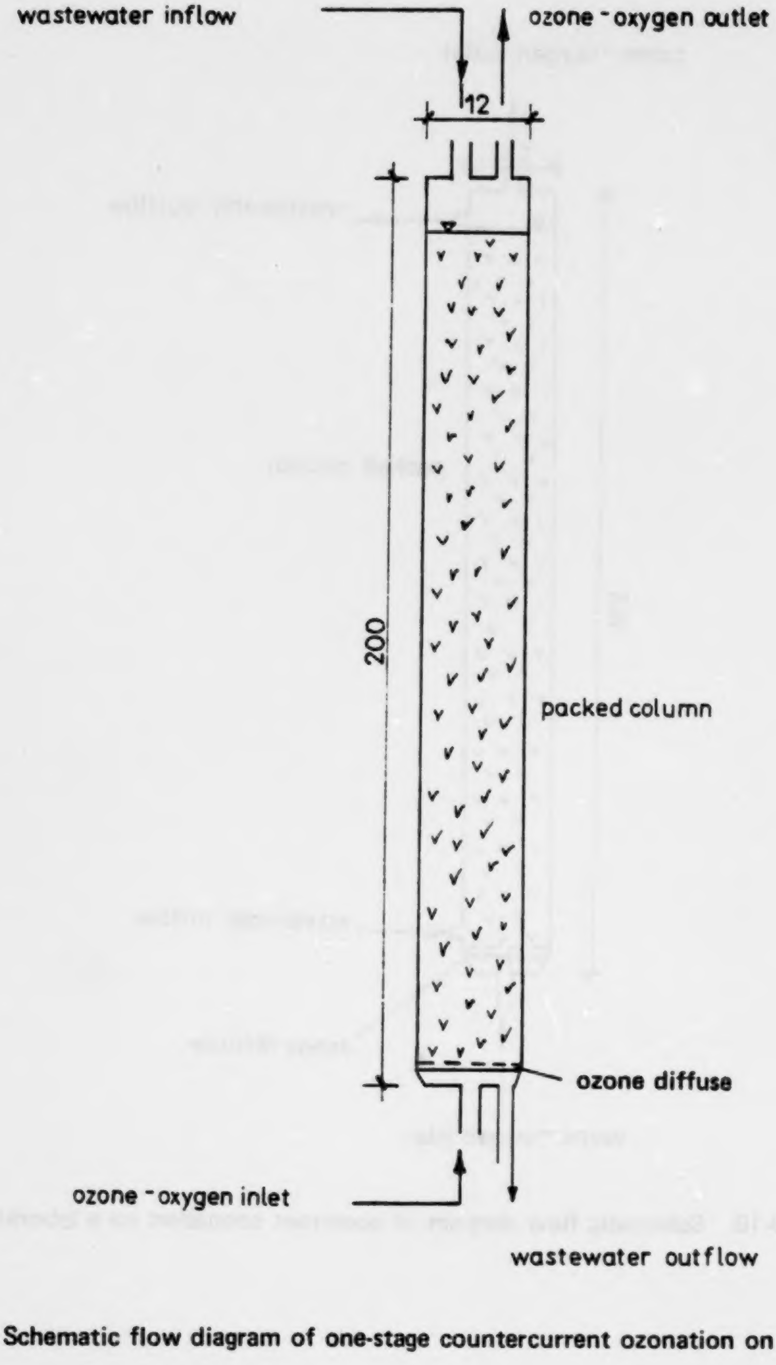

wastewater inflow
ozone - oxygen outlet
12
200
packed column
ozone diffuse
ozone - oxygen inlet
wastewater outflow

Figure 9-11. Schematic flow diagram of one-stage countercurrent ozonation on a pilot scale.

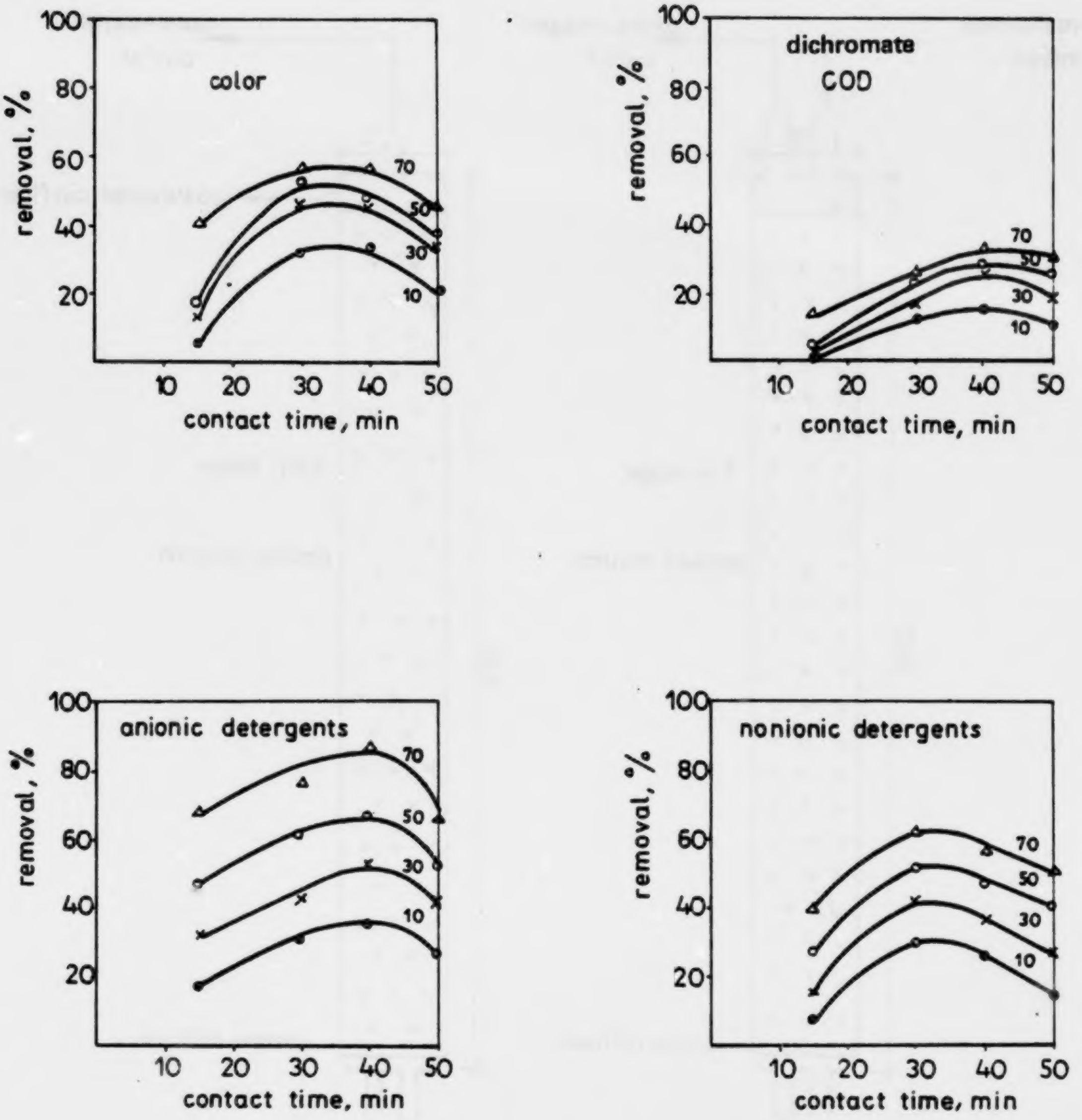


Figure 9-12. Removal of contaminants in a one-stage continuous countercurrent column using 10, 30, 50, and 70 mg/l ozone doses.

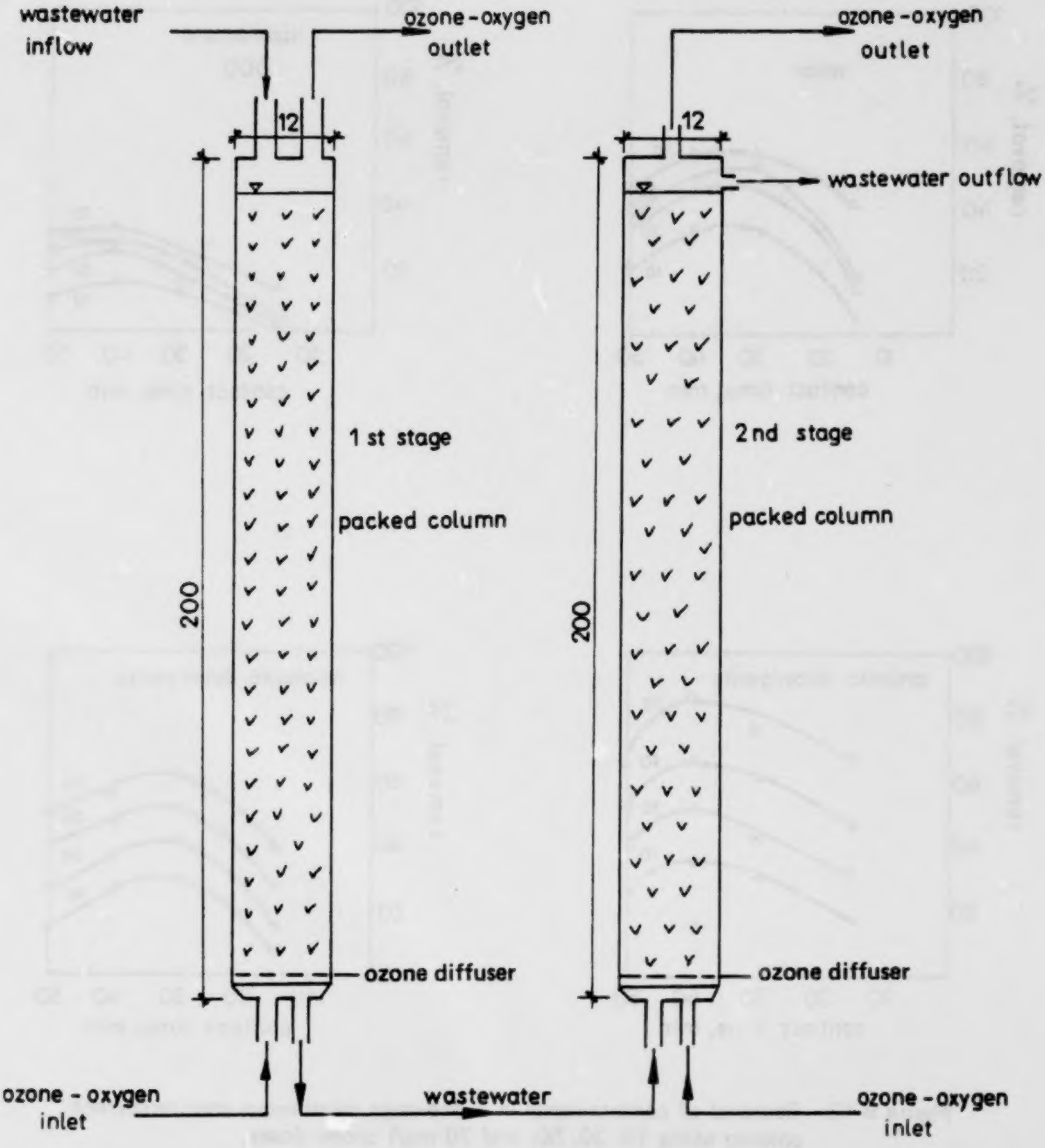

wastewater inflow
ozone-oxygen outlet
12
200
1 st stage
packed column
ozone diffuser
ozone - oxygen inlet
wastewater
ozone-oxygen outlet
12
wastewater outflow
200
2nd stage
packed column
ozone diffuser
ozone-oxygen inlet

Figure 9-13. Schematic flow diagram of double-stage ozonation on a pilot scale.

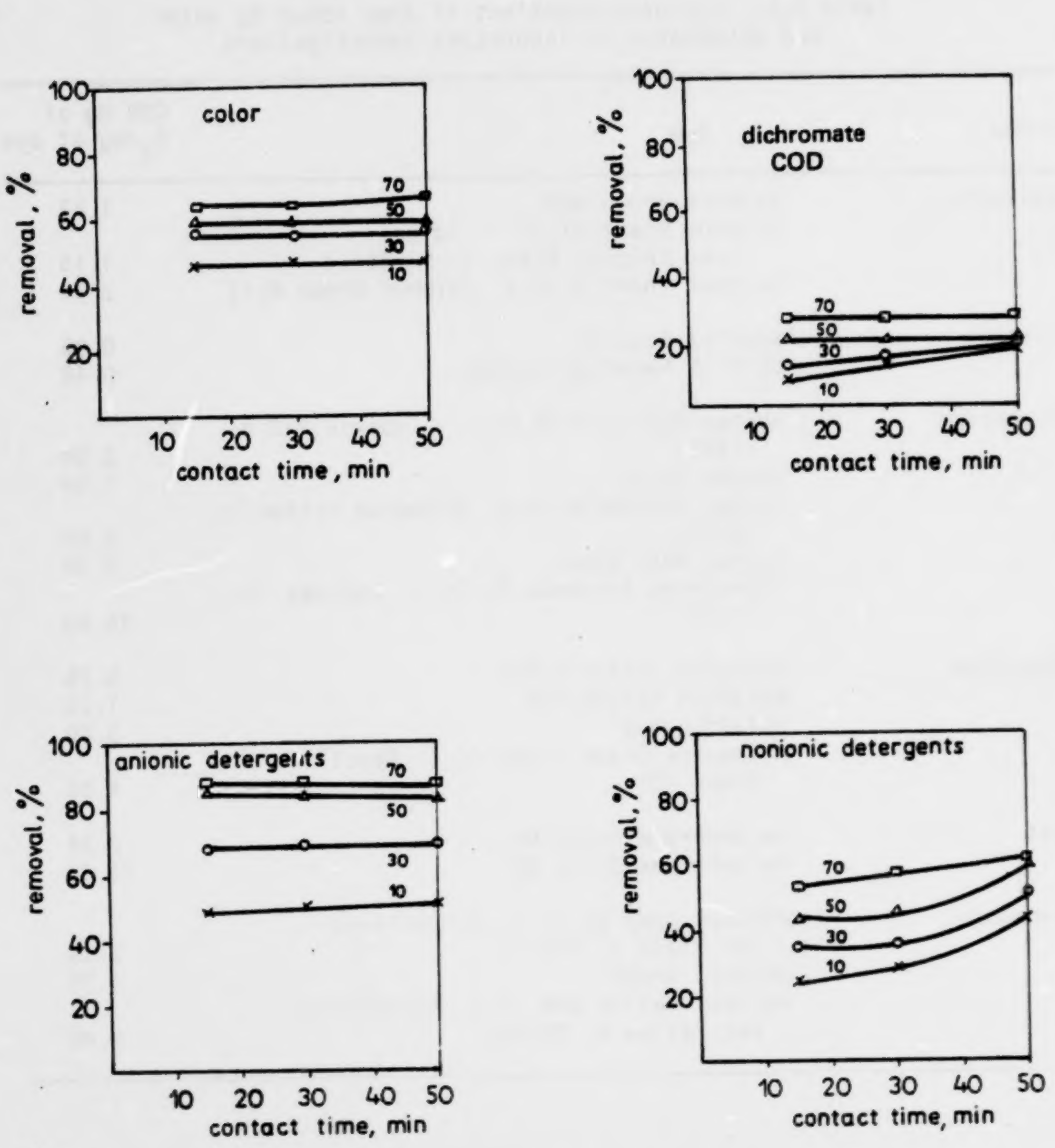


Figure 9-14. Removal of contaminants in double-stage continuous columns using 10, 30, 50, and 70 mg/l ozone doses.

Table 9.1. COD determinations of dyes added to water and wastewater in laboratory investigations

Group	Dye	COD mg of O_2/mg of dye
Sulfuric	Sulphur Brown W4R	1.53
	Sulphur Black WT (C.I. Solubilised Sulphur Black 1; 53186)	1.15
	Sulphur Khaki G (C.I. Sulphur Green 8:1)	2.44
Glacial	Scarlet Base RG	0.95
	Salt of Naphthanil Blue	0.48
Dispersed	Synten Rubine P-3B (C.I. Disperse Red 5; 11215)	2.50
	Synten Azure	1.54
	Synten Yellow 5G (C.I. Disperse Yellow 5; 12790)	6.50
	Synten Navy Blue	7.30
	Indanthren Bordeaux RR (C.I. Vat Red 15; 71100)	26.80
Reactive	Helaktyn Yellow D-5GN	5.75
	Helaktyn Yellow DGR	1.22
	Helaktyn Red	5.40
	Drimarene Green X-2BL (C.I. Reactive Green 15)	4.36
Vat	Helanthrene Green B5	2.24
	Helanthrene Olive BT	21.80
Indigosol	Helasol Gray BL (C.I. Solubilised Vat Black 1; 73671)	3.16
	Helasol Green	4.75
	Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106)	9.45

Table 9-2. Single dyes used in ozone oxidation investigations

No.	Group	Dye*
1	Glacial	Scarlet Base RG
2	Glacial	Salt of Naphthanil Blue
3	Dispersed	Synten Rubine P-3B
4	Dispersed	Synten Azure
5	Dispersed	Synten Navy Blue P-B2
6	Dispersed	Indanthren Bordeaux RR
7	Reactive	Helaktyn Yellow D-5GN
8	Reactive	Helaktyn Yellow DGR
9	Reactive	Helaktyn Red F5B
10	Reactive	Drimarene Green X-2BL
11	Vat	Helanthrene Green B5
12	Vat	Helanthrene Olive BT
13	Indigosol	Helasol Green 2G
14	Indigosol	Helasol Yellow GOK
15	Sulfuric	Sulphur Brown W4R
16	Sulfuric	Sulphur Black WT
17	Sulfuric	Sulphur Khaki G

*See pages 12 and 13 for available Colour Index information on each of these dyes.

Table 9-3. Technical parameters and ozone balance in the ozone oxidation process of water dye solutions

Group of dyes	Name of dye	Ozonation time, min	Air-ozone mixture flow, l/h	Ozone concentration in air supplied, mg/l	Total amount of ozone introduced, mg	Ozone balance, %		
						Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
Glacial	Scarlet Base RG	5	15.0	13.3	16.6	44.4	24.8	30.8
		10	10.8	13.3	23.9	56.7	7.2	36.1
		12	10.8	13.3	28.7	58.6	3.6	37.8
	Salt of Naphthanil Blue BT	2	18.6	12.7	7.8	58.8	13.7	27.5
		4	18.0	12.7	15.2	58.2	7.2	34.6
		11	16.8	12.7	39.1	52.6	2.3	45.1
Dispersed	Synten Rubine P-3B	5	12.6	11.1	11.6	37.3	21.3	41.4
		10	12.6	11.1	23.3	42.4	5.4	52.2
		20	13.2	11.1	48.8	21.4	4.0	74.6
	Synten Azure S	5	12.0	11.1	11.1	48.1	13.0	38.9
		10	12.6	11.1	23.3	41.4	5.2	53.4
		15	12.6	11.1	34.9	34.6	2.6	62.8
		33	12.6	11.1	76.9	35.5	0.9	63.6
	Synten Navy-Blue P-BL	30	7.2	11.4	41.0	36.2	13.9	49.9
		43	6.6	11.4	53.9	42.6	3.1	54.3
	Indanthren Bordeaux RR	20	10.8	12.7	45.7	41.3	3.9	54.8
		40	7.8	12.7	66.0	43.4	2.3	54.3
		120	7.8	12.7	198.1	17.2	0.5	82.3

Table 9-3 (con.)

Group of dyes	Name of dye	Ozonation time, min	Air Ozone mixture flow, l/h	Ozone concentration in air supplied mg/l	Total amount of ozone, introduced, mg	Ozone balance, %		
						Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
Reactive	Helaktyn Yellow D - 5GN	5	8.4	10.7	7.5	51.8	19.3	28.9
		10	8.4	10.7	14.9	59.9	5.7	34.4
		23	7.2	10.7	29.5	54.6	4.0	41.4
	Helaktyn Yellow DGR	20	7.8	13.1	34.0	40.3	9.8	49.3
		23	7.8	13.1	39.1	47.1	3.6	49.3
	Helaktyn Red F5B	20	8.4	12.7	35.5	50.9	6.9	42.2
		22	8.4	12.7	39.1	55.6	3.9	40.5
	Drimarene Green X- 2BL	10	8.4	14.5	20.3	50.1	14.3	35.6
		20	7.8	14.5	37.7	36.9	5.7	57.4
		40	6.6	14.5	63.8	50.9	2.3	46.8
Vat	Helanthrene Green BS	5	6.6	12.7	6.9	36.7	35.9	27.4
		10	7.8	12.7	16.5	45.1	8.7	46.2
		20	10.2	12.7	43.1	48.6	5.5	45.9
		40	7.8	12.7	66.0	50.9	0.4	48.7
	Helanthrene Olive BT	30	4.2	12.9	27.0	44.5	9.7	45.8
		60	4.2	12.9	54.1	46.8	2.0	51.2
		120	4.2	12.9	108.3	39.8	0.7	59.5

Table 9-3 (con.)

Group of dyes	Name of dye	Ozonation time, min	Air Ozone mixture flow, l/h	Ozone concentration in air supplied mg/l	Total amount of ozone, introduced mg	Ozone balance,% Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
Indigosol	Helasol Green ZG	10	11.4	12.0	22.8	28.7	19.8	51.5
		15	9.0	12.0	27.0	28.3	6.6	65.1
	Helasol Yellow GOK	20	6.6	11.9	26.1	14.4	40.4	45.2
		71	6.6	11.9	92.9	36.2	1.8	62.0
Sulfuric	Sulphur Brown W4R	5	10.2	11.0	9.3	42.2	7.7	50.1
		10	9.6	11.0	17.6	34.7	5.9	59.4
		15	10.8	11.0	29.7	25.9	3.0	71.1
	Sulphur Black WT	5	7.2	14.7	8.8	40.1	17.7	42.1
		10	8.4	14.7	20.5	27.6	12.3	69.1
		15	7.2	14.7	26.9	21.6	8.6	69.8
	Sulphur Khaki G	5	13.8	11.7	13.5	34.2	22.8	43.0
		15	13.6	11.7	39.8	31.0	3.8	65.2

Table 9-4. Effectiveness of ozone oxidation of water dye solutions

Group of dye	Name of dye	pH	Ozonation contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of utilized ozone, mg O_3/mg of dye	Color removal, %	Color threshold	Dichromate COD concentration, mg O_2/l	Dichromate COD removal, %
Glacial	Scarlet Base RG	7.20	0	-	-	-	-	3.1/100	26.3	-
		7.30	5	7.45	0.456	0.198	45.0	5.0/100	26.3	0.0
		7.35	10	13.39	0.645	0.355	65.5	10/100	23.2	11.8
		7.45	130	17.14	0.780	0.457	84.0	24/100	18.2	30.8
	Salt of Naphthanil Blue BT	7.45	0	-	-	-	-	0.4/100	36.4	-
		7.45	2	4.63	0.210	0.124	21.3	0.8/100	37.4	0.0
		7.45	4	8.88	0.407	0.237	56.5	2.5/100	30.3	16.8
		7.45	11	21.33	1.036	0.570	96.7	24/100	22.2	39.0
Dispersed	Synten Rubine P-3B	7.70	0	-	-	-	-	1.0/100	64.6	-
		7.85	5	4.43	0.317	0.118	15.2	2.0/100	58.6	9.3
		7.90	10	10.12	0.636	0.270	25.6	2.6/100	56.6	12.4
		7.75	20	10.36	1.288	0.276	37.2	3.2/100	48.5	24.9
	Synten Azure S	7.55	0	-	-	-	-	3.0/100	74.6	-
		7.58	5	5.34	0.296	0.142	31.0	3.5/100	72.4	2.9
		7.55	10	9.88	0.636	0.264	43.2	4.7/100	60.5	18.9
		7.60	15	12.10	0.932	0.323	52.2	10/100	57.1	23.4
		7.55	33	27.54	2.070	0.735	68.1	2.5/100	43.9	41.2

Table 9-4 (con.)

Group of dye	Name of dye	pH	Ozonation contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of utilized ozone, mg O_3/mg of dye	Color removal, %	Color threshold	Dichromate COD concentration, mg O_2/l	Dichromate COD removal, %
Dispersed (con.)	Synten Navy Blue P-BL	7.65	0	-	-	-	-	4.0/100	28.3	-
		7.70	30	15.99	1.140	0.427	63.0	11/100	21.7	23.4
		7.70	43	21.84	1.370	0.583	98.8	18/100	19.6	30.8
	Indanthren Bordeaux RR	7.75	0	-	-	-	-	1.1/100	71.8	-
		7.90	20	19.30	1.246	0.514	24.1	1.5/100	77.4	0.0
		7.85	40	28.08	1.730	0.750	31.4	2.3/100	44.3	38.3
		8.10	120	34.42	5.490	0.916	94.5	55/100	13.2	81.7
Reactive	Helaktyn Yellow D-5GN	7.80	0	-	-	-	-	0.5/100	29.1	-
		7.70	5	3.87	0.199	0.103	38.8	1.0/100	37.6	0.0
		7.60	10	9.42	0.419	0.262	58.8	2.2/100	23.7	18.6
		7.60	23	16.97	0.804	0.452	90.2	18/100	22.6	22.4
	Helaktyn Yellow DGR	7.53	0	-	-	-	-	0.2/100	25.3	-
		7.57	20	13.94	0.921	0.372	80.1	4.2/100	19.4	23.4
		7.63	93	19.56	1.107	0.521	93.3	23/100	15.5	33.8
	Helaktyn Red P5B	7.80	0	-	-	-	-	0.18/100	19.6	-
		7.60	20	18.33	0.965	0.485	89.0	5.0/100	38.3	0.0
		7.75	22	20.51	0.982	0.547	98.0	35/100	12.8	34.7

Table 9-4 (con.)

Group of dye	Name of dye	pH	Ozonation contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of utilized ozone, mg O_3/mg of dye	Color removal, %	Color threshold	Dichromate COD concentration, mg O_2/l	Dichromate COD removal, %
Reactive (con.)	Drimarene Green	8.05	0	-	-	-	-	0.43/100	21.7	-
		8.15	10	10.30	0.549	0.275	33.8	0.45/100	23.6	0.0
		8.10	20	10.48	0.757	0.280	68.2	2.2/100	17.0	21.7
		8.15	40	33.38	3.750	0.890	90.5	11/100	10.4	52.1
Vat	Helanthrene Green BS	8.50	0	-	-	-	-	0.45/100	82.0	-
		8.50	5	2.57	0.187	0.059	0.0	0.45/100	78.1	4.7
		8.30	10	7.76	0.456	0.207	1.6	0.45/100	76.9	6.2
		8.20	20	17.03	0.928	0.454	5.6	0.46/100	71.2	13.2
		8.15	90	77.28	4.050	2.060	41.2	0.50/100	19.1	76.7
	Helanthrene Olive BT	7.85	0	-	-	-	-	2.0/100	67.2	-
		7.80	30	12.33	0.748	0.324	23.2	3.0/100	47.7	29.0
		7.75	60	25.82	1.497	0.688	23.2	3.5/100	47.7	29.0
		7.70	120	46.26	3.950	1.233	78.5	8.5/100	25.4	62.2
Indigosol	Helasol Green ZG	7.80	0	-	-	-	-	20/100	13.1	-
		7.85	10	6.54	0.708	0.175	46.9	25/100	5.60	57.2
		7.90	15	7.80	0.736	0.208	89.0	48/100	5.60	57.2
	Helasol Yellow GOK	7.90	0	-	-	-	-	0.25/100	37.8	-
		8.05	20	3.96	0.736	0.106	56.1	1.0/100	34.0	10.1
		8.00	71	34.07	2.501	0.910	97.5	30/100	7.6	79.9

Table 9-4 (con.)

Group of dye	Name of dye	pH	Ozonation contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of utilized ozone, mg O_3/mg of dye	Color removal, %	Color threshold	Dichromate COD concentration, mg O_2/1	Dichromate COD removal, %
Sulfuric	Sulphur Brown W4R	-	0	-	-	-	-	20/100	6.54	-
		-	5	3.95	0.250	0.105	32.8	70/100	9.81	0.0
		-	10	6.27	0.484	0.166	72.0	69/100	-	-
		-	15	7.68	0.791	0.205	50.2	67/100	7.63	0.0
	Sulphur Black WT	7.55	0	-	-	-	-	68/100	1.03	-
		7.70	5	3.65	0.243	0.097	76.2	15/100	2.06	0.0
		7.70	10	5.66	0.549	0.151	76.2	100/100	1.03	0.0
		7.75	15	5.99	0.733	0.158	76.2	100/100	1.03	0.0
	Sulphur Khaki G	7.67	0	-	-	-	-	32/100	3.3	-
		7.67	5	4.58	0.357	0.122	86.3	90/100	4.4	0.0
		7.80	15	12.29	1.060	0.328	86.3	100/100	3.3	0.0

Table 9-5. Dyes fed into biologically treated wastewater

No.	Group	Dye*
1.	Glacial	Scarlet Base RG
2.	Glacial	Salt of Naphthanil Blue BT
3.	Dispersed	Synten Rubine P-3B
7.	Reactive	Helaktyn Yellow D-5GN
9.	Reactive	Helaktyn Red F5B
15.	Sulfuric	Sulphur Brown W4R
16.	Sulfuric	Sulphur Black WT
11.	Vat	Helanthrene Green B5
13.	Indigosol	Helasol Green ZG

*See pages 12 and 13 for available Colour Index information on each of these dyes.

Table 9-6. Effectiveness of ozone oxidation of biologically treated wastewater with the addition of individual dyes and dye mixtures

Group of dyes or number of mixtures	Name of dye	pH	Turbidity, mg SiO_2/l	Conductivity, S cm^{-1}	Contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of ozone utilized, mg O_3/mg of dye	Color removal, %
	Biologically treated wastewater without the addition of dye	7.95	5	820	-	-	-	-	-
		8.10	5	841	5	7.09	0.507	0.139	39.8
		8.15	5	853	10	8.60	1.013	0.229	58.7
		8.15	5	850	20	12.34	2.133	0.329	74.8
		8.35	5	848	40	17.52	2.773	0.467	68.9
Glacial	Scarlet Base RG	7.60	5	891	-	-	-	-	-
		7.75	5	884	5	0.34	0.60	0.0224	0.0
		7.90	5	881	10	1.20	0.346	0.0320	68.3
		7.80	5	887	17	3.80	0.661	0.101	68.3
		7.80	5	903	24	8.22	1.024	0.219	75.4
	Salt of Naphthanil Blue BT	7.50	-	922	-	-	-	-	-
		7.75	-	898	9	4.89	0.226	0.130	36.7
		7.75	-	898	14	8.29	0.347	0.221	51.7
		7.85	-	893	46	22.53	1.210	0.601	97.5
Dispersed	Synten Rubine P-3B	7.75	-	885	-	-	-	-	-
		8.00	-	872	20	8.30	0.496	0.221	18.5
		7.95	-	870	40	19.83	1.086	0.529	37.9
		8.00	-	874	90	29.78	2.048	0.794	57.3
	Helaktyn Yellow D5GN	8.0	10	881	-	-	-	-	-
		8.10	5	899	5	3.58	0.252	0.0955	27.5
		7.95	5	877	15	8.88	0.864	0.237	84.3
		7.80	5	888	18	10.20	1.123	0.272	90.2
		8.00	5	896	25	15.40	1.400	0.411	92.8

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	pH	Turbidity, mg SiO_2/l	Conductivity, S cm^{-1}	Contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of ozone utilized, mg O_3/mg of dye	Color removal, %
Reactive									
		7.55	-	851	-	-	-	-	-
	Helaktyn Red F - 5B	7.95	-	823	18	8.47	0.403	0.226	48.7
		7.90	-	825	25	12.69	0.557	0.338	73.3
		8.00	-	811	48	20.44	1.058	0.545	96.3
		7.73	10	911	-	-	-	-	-
	Sulphur Brown W4R	8.05	5	862	5	3.22	0.300	0.086	18.1
		8.00	5	897	10	6.10	0.881	0.163	-
Sulfuric		8.10	5	892	20	8.28	1.440	0.221	11.6
		7.50	-	856	-	-	-	-	-
	Sulphur Black WT	7.90	-	849	10	5.35	0.236	0.147	41.2
		7.95	-	873	20	9.31	0.466	0.248	63.6
		8.05	-	864	47	16.10	1.098	0.429	69.7
		8.20	8	1390	-	-	-	-	-
	Biologically treated wastewater without the addition of dye	8.35	8	1280	5	2.85	0.142	0.076	6.6
		8.30	-	1365	10	5.62	0.339	0.150	17.7
		8.30	5	1390	20	9.48	0.584	0.253	17.7
		8.25	5	1340	40	18.19	1.279	0.485	22.2
		8.25	-	1455	-	-	-	-	-
Vat	Helanthrene Green BS	8.20	-	1365	80	33.35	2.039	0.889	-
		8.15	-	1390	120	51.65	3.076	1.377	9.7

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	pH	Turbidity,	Conductivity,	Contact time,	Ozone used and decomposed by the sample,	Amount of ozone introduced,	Amount of ozone utilized,	Color removal,
			mg SiO_2/l	S cm^{-1}	min	mg	mg O_3/mg of dye	mg O_3/mg of dye	%
		8.20	-	1415	-	-	-	-	-
Indigosol	Helasol Green ZG	8.35	-	1400	15	6.16	0.339	0.164	11.0
		8.30	-	1395	19	7.46	0.435	0.199	14.3
		8.45	-	1415	96	25.86	2.149	0.690	28.0
		8.10	-	1482	-	-	-	-	-
Mixture I	Salt of Naphthanil	8.20	-	1526	10	4.74	1.067	0.042	10.5
	Blue BT	8.30	-	1506	50	23.05	0.337	0.205	25.3
	Helanthrene Green BS	8.30	-	1492	180	57.43	1.216	0.511	38.4
	Sulphur Black WT	7.80	-	1535	-	-	-	-	-
Mixture II	Scarlet Base RG	8.25	-	1500	10	3.24	0.081	0.029	3.1
	Helaktyn Red F5B	8.20	-	1510	20	9.84	0.181	0.087	18.3
		8.25	-	1490	50	40.38	0.491	0.359	72.3
		8.25	-	1520	82	62.10	0.853	0.552	91.2
	Helasol Green ZG	8.20	-	1560	-	-	-	-	-
Mixture III	Indanthren Bordeaux RR	8.30	-	1530	15	8.15	0.128	0.072	5.0
	Helaktyn Yellow	8.25	-	1540	30	13.68	0.256	0.122	15.4
		8.25	-	1505	60	25.68	0.491	0.228	30.6
		8.20	-	1490	180	69.22	1.440	0.615	50.5
	Synten Azure	8.40	-	1400	-	-	-	-	-
Mixture IV	Helasol Yellow GOK	8.40	-	1496	20	13.68	0.163	0.121	15.2
	Drimarene Green	8.40	-	1394	40	24.45	0.336	0.217	23.5
		8.40	-	1416	60	28.23	0.490	0.251	31.5
		8.40	-	1466	180	81.21	1.594	0.722	64.6

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	pH	Turbidity, mg SiO_2/l	Conductivity, S cm^{-1}	Contact time, min	Ozone used and decomposed by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of ozone utilized, mg O_3/mg of dye	Color removal, %
		8.40	-	1506	-	-	-	-	-
Mixture V	Helaktyn Yellow D5GH	8.40	-	1454	5	2.58	0.034	0.023	9.0
	Helasol Grey BL	8.40	-	1464	10	6.24	0.072	0.056	23.5
		8.40	-	1590	15	9.99	0.110	0.089	33.3
		8.40	-	1496	60	33.99	0.499	0.302	76.9

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	Color threshold	Dichromate COD, mgO_2/l	Dichromate COD removal, %	Anionic detergents, mg/l	Removal of anionic detergents, %	Nonionic detergents, mg/l	Removal of nonionic detergents, %	TOC, mg/l	Removal of TOC, %	Removal of color Mean light transmittance in the range of 360 to 650 nm %
	Biologically treated wastewater without the addition of dye	36/100	62.4	-	0.40	-	4.0	-	16.0	-	-
		66/100	62.4	0.0	0.19	52.5	3.6	10.0	12.0	25.0	-
		77/100	37.6	39.7	0.17	57.5	3.0	25.0	11.0	31.2	-
		76/100	37.6	39.7	0.17	57.5	1.45	63.7	8.5	46.9	-
		70/100	29.1	53.4	0.22	45.0	1.0	75.0	8.5	46.9	-
Glacial	Scarlet Base RG	2.0/100	55.7	-	-	-	-	-	28.3	-	-
		2.5/100	48.0	13.8	-	-	-	-	20.5	27.6	-
		8.0/100	44.8	19.6	-	-	-	-	18.0	36.4	-
		15/100	41.7	25.1	-	-	-	-	17.5	38.2	-
		15/100	16.0	71.3	-	-	-	-	16.5	41.7	-
	Salt of Naphthanil Blue BT	0.35/100	46.9	-	-	-	-	-	30.0	-	-
		1.0/100	43.9	6.40	-	-	-	-	19.0	36.7	-
		2.0/100	45.5	3.0	-	-	-	-	15.0	50.0	-
		29/100	29.3	37.5	-	-	-	-	15.0	50.0	-
Dispersed	Synten Rubine P-3B	0.4/100	92.1	-	-	-	-	-	32.0	-	-
		1.1/100	79.7	13.5	-	-	-	-	17.0	46.9	-
		1.5/100	76.5	16.9	-	-	-	-	17.0	46.9	-
		2.5/100	55.3	40.0	-	-	-	-	17.0	46.9	-

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	Color threshold	Dichromate COD, mgO_2/l	Dichromate COD removal %	Anionic detergents, mg/l	Removal of anionic detergents, %	Nonionic detergents, mg/l	Removal of nonionic detergents, %	TOC, mg/l	Removal of TOC, %	Removal of color Mean light transmittance in the range of 360 to 650 nm %
Reactive	Helaktyn Yellow D5GH	0.4/100	51.2	-	-	-	-	-	80.0	-	-
		0.9/100	54.4	-	-	-	-	-	20.5	74.4	-
		16/100	60.8	-	-	-	-	-	19.5	75.6	-
		24/100	96.0	-	-	-	-	-	13.5	83.1	-
		43/100	32.0	37.5	-	-	-	-	13.0	83.7	-
	Helaktyn Red F-5B	0.18/100	43.2	-	-	-	-	-	21.0	-	-
		1.1/100	33.6	22.2	-	-	-	-	17.0	19.0	-
		2.25/100	30.4	29.6	-	-	-	-	15.5	26.2	-
		12/100	27.2	37.0	-	-	-	-	11.0	47.6	-
Sulfuric	Sulphur Brown W4R	19/100	12.8	-	-	-	-	-	16.5	-	-
		25/100	16.0	-	-	-	-	-	10.5	36.4	-
		24/100	19.2	-	-	-	-	-	9.5	42.4	-
		28/100	25.6	-	-	-	-	-	7.5	54.5	-
	Sulphuric Black WT	20/100	27.8	-	-	-	-	-	27.5	-	-
		43/100	29.6	-	-	-	-	-	9.5	65.5	-
		59/100	25.9	6.8	-	-	-	-	9.5	65.5	-
		74/100	13.0	53.2	-	-	-	-	7.0	74.5	-

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	Color threshold	Dichromate COD, mgO_2/l	Dichromate COD removal, %	Anionic detergents, mg/l	Removal of anionic detergents, %	Nonionic detergents, mg/l	Removal of nonionic detergents, %	TOC, mg/l	Removal of TOC, %	Removal color Mean light transmittance in the range of 360 to 650 nm %
	Biologically treated wastewater without the addition of dye	10.0/100	-	-	0.81	-	4.60	-	18.0	-	-
		15/100	-	-	0.65	19.75	4.35	5.4	17.5	2.8	-
		21/100	-	-	0.49	39.5	4.00	13.0	13.0	27.8	-
		25/100	-	-	0.38	53.1	3.50	23.9	13.0	27.8	-
		30/100	-	-	0.28	65.4	3.30	28.3	11.5	36.1	-
		0.34/100	129.0	-	-	-	-	-	35.0	-	-
Vat	Helanthrene Green BS	0.30/100	109.6	15.0	-	-	-	-	26.0	25.7	-
		0.36/100	86.0	33.3	-	-	-	-	21.0	40.0	-
		14/100	51.0	-	-	-	-	-	18.0	-	-
Indigosol	Helasol Green ZG	23/100	41.2	19.2	-	-	-	-	16.0	11.1	-
		23/100	43.2	15.3	-	-	-	-	15.5	13.9	-
		30/100	39.2	23.1	-	-	-	-	15.0	16.7	-
	Salt of Naphthanil	0.55/100	151.6	-	-	-	-	-	42.5	-	36.6
Mixture I	Blue BT	0.55/100	138.0	8.9	-	-	-	-	39.5	7.1	43.2
	Helanthrene Green BS	0.57/100	140.0	7.6	-	-	-	-	34.5	18.8	52.6
		0.57/100	90.0	40.6	-	-	-	-	34.5	18.8	60.9

Table 9-6 (con.)

Group of dyes or number of mixtures	Name of dye	Color threshold	Dichromate COD, mgO_2/l	Dichromate COD removal, %	Anionic detergents, mg/l	Removal of anionic detergents, %	Nonionic detergents, mg/l	Removal of nonionic detergents, %	TOC, mg/l	Removal of TOC, %	Removal of color Mean light transmittance in the range of 360 to 650 nm %
	Sulphur Black WT	0.14/100	106.0	-	-	-	-	-	34.5	-	36.1
Mixture II	Scarlet Base RG	0.21/100	93.8	11.5	-	-	-	-	30.0	13.0	38.1
	Helaktyn Red F5B	0.53/100	93.8	11.5	-	-	-	-	30.0	13.0	47.8
		3.3/100	73.4	30.2	-	-	-	-	28.0	18.8	82.3
		13.2/100	65.2	38.5	-	-	-	-	24.5	29.0	94.4
	Helasol Green ZG	1.5/100	105.8	-	-	-	-	-	30.0	-	48.1
Mixture III	Indanthren Bordeaux RR	1.9/100	98.0	7.4	-	-	-	-	27.0	10.0	50.7
		1.1/100	102.0	3.6	-	-	-	-	25.0	16.7	56.1
	Helaktyn Yellow	1.4/100	84.4	20.2	-	-	-	-	23.5	21.7	64.0
		2.0/100	62.8	40.6	-	-	-	-	21.5	28.3	74.3
		0.34/100	156.0	-	-	-	-	-	40.0	-	31.4
Mixture IV	Synten Azure	0.64/100	138.0	11.5	-	-	-	-	38.5	3.7	41.8
	Helasol Yellow GOK	0.64/100	142.0	8.9	-	-	-	-	32.0	20.0	47.5
	Drimarene Green	0.52/100	124.0	20.5	-	-	-	-	30.0	25.0	52.9
		0.60/100	96.0	38.5	-	-	-	-	30.0	25.0	75.6
		0.54/100	68.0	-	-	-	-	-	26.5	-	-
Mixture V	Helaktyn Yellow D5GH	0.70/100	68.0	0.0	-	-	-	-	23.0	13.2	-
	Helasol Grey	1.1/100	70.0	-	-	-	-	-	22.5	15.1	-
		1.1/100	66.0	2.9	-	-	-	-	22.0	17.0	-
		9.5/100	48.0	29.4	-	-	-	-	20.5	22.6	-

Table 9-7. Technical parameters and ozone balance in the ozone oxidation process applied to biologically treated wastewaters with the addition of individual dyes and dye mixtures

Dye group or no. of mixture	Name of dye	Ozonation time, min	Air-ozone mixture, l/h	Ozone concentration in air supplied, mg/l	Total amount of ozone introduced, mg	Ozone balance, %		
						Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
-	Biologically treated wastewater without the addition of dye	5	11.40	20.0	19.0	37.3	3.3	59.4
		10	11.40	20.0	38.0	22.6	2.4	74.5
		20	12.00	20.0	80.0	15.4	2.1	82.5
		40	7.80	20.0	104.0	16.8	1.9	81.3
Glacial	Scarlet Base RG	5	3.60	20.0	6.0	14.0	6.0	80.0
		10	3.60	21.6	12.2	9.3	0.0	90.7
		17	5.40	21.6	33.0	15.3	2.4	82.3
		24	5.40	20.0	43.2	21.4	11.7	66.9
	Salt of Naphthanil Blue BT	9	4.80	11.64	8.4	57.6	17.0	25.4
		14	4.80	11.64	13.0	63.6	12.4	24.0
		46	4.80	11.64	42.8	49.6	2.8	47.6
Dispersed	Synten Rubine P-3B	20	4.80	11.64	18.6	44.6	3.9	51.5
		40	4.80	11.64	37.2	48.7	2.4	48.9
		90	4.20	11.64	73.3	38.8	0.0	61.2
Reactive	Helaktyn Yellow D-5GN	5	5.40	21.0	9.4	37.9	6.7	55.4
		15	6.0	21.6	32.4	27.4	0.0	72.6
		18	6.0	21.6	38.9	24.2	1.7	74.1
		25	6.0	21.0	52.5	29.3	2.1	88.6

Table 9-7 (con.)

Dye group or no. of mixture	Name of dye	Ozonation time, min	Air-ozone mixture, l/h	Ozone concentration in air supplied, mg/l	Total amount of ozone introduced, mg	Ozone balance, %		
						Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
Reactive (con.)	Helaktyn Red F5B	18	4.80	10.44	15.0	56.0	6.0	38.0
		25	4.80	10.44	20.9	60.8	4.7	34.5
		48	4.80	10.44	40.1	51.5	0.7	47.8
Sulfuric	Sulphur Brown W4R	5	6.60	20.1	11.1	28.6	3.1	68.3
		10	9.00	21.6	32.4	18.5	1.6	79.9
		20	7.20	21.6	51.8	15.3	2.0	82.7
	Sulphur Black WT	10	4.20	12.48	8.7	62.4	5.1	32.5
		20	4.20	12.48	17.5	53.3	4.1	42.6
		47	4.20	12.48	41.2	39.1	2.6	58.3
-	Biologically treated wastewater without the addition of dye	5	4.80	12.96	5.2	53.7	30.5	15.8
		10	5.40	12.96	11.7	44.2	14.2	41.6
		20	4.80	12.96	20.7	43.3	7.4	49.3
		40	5.40	12.96	46.6	37.9	4.5	57.6
Vat	Helanthrene Green BS	80	4.20	12.96	72.6	43.6	2.7	53.7
		120	4.20	12.96	108.9	44.8	1.3	53.9
Indigosol	Helasol Green ZG	15	4.20	12.36	12.9	48.4	12.0	39.6
		19	4.20	12.36	16.3	45.7	11.6	42.7
		96	4.20	12.36	83.1	32.1	3.6	64.3

Table 9-7 (con.)

Dye group or no. of mixture	Name of dye	Ozonation time, min	Air-ozone mixture, l/h	Ozone concentration in air supplied, mg/l	Total amount of ozone introduced, mg	Ozone balance, %		
						Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
Mixture I	Salt of Naphthanil Blue BT Helanthrene Green BS	10	4.20	10.32	7.5	63.0	17.9	19.1
		50	4.20	10.32	36.1	60.9	4.3	34.8
		180	4.20	10.32	130.0	42.0	0.8	57.2
Mixture II	Sulphur Black WT Scarlet Base RG Helaktyn Red F5B	10	5.40	12.0	10.8	35.5	59.2	5.3
		20	5.40	12.0	21.6	48.2	44.1	7.7
		50	5.40	12.0	54.0	73.2	5.5	21.3
		83	5.40	12.0	89.6	64.7	2.1	33.2
Mixture III	Helasol Green ZG Indanthren Bordeaux RR Helaktyn Yellow DGR	15	4.80	12.0	14.4	57.2	9.4	33.4
		30	4.80	12.0	28.8	47.5	7.5	45.0
		60	4.80	12.0	57.6	46.5	2.6	50.9
		180	4.80	12.0	172.8	42.8	0.9	56.3
Mixture IV	Synten Blue Helasol Yellow GOK Drimarene Green	20	4.80	10.80	17.3	74.0	6.4	19.6
		40	4.80	10.80	34.5	64.7	3.6	31.7
		60	4.80	10.80	51.8	51.3	3.4	45.3
		180	5.40	10.80	174.9	45.3	0.8	53.9
Mixture V	Helaktyn Yellow D-5GN Helasol Grey	5	4.20	10.80	3.8	68.3	19.0	12.7
		10	4.20	10.80	7.6	77.0	11.1	11.9
		15	4.20	10.80	11.3	80.4	8.0	11.6
		60	4.20	10.80	45.4	60.5	2.4	37.1

Table 9-8. Technical parameters and ozone balance in the oxidation process applied to biologically treated wastewaters with the addition of individual dyes of different concentrations

Group of dye	Name of dye	Concentration of dye, mg/l	Contact time, min	Air-ozone mixture, l/h	Ozone concentration in air supplied, mg/l	Total amount of ozone introduced, mg	Ozone balance, %		
							Ozone used and decomposed by the sample	Ozone unreacted	Ozone in exit gas
-	Biologically treated wastewater without the addition of dye	-	5	6.6	11.89	6.53	34.6	39.2	26.2
		-	10	6.6	11.89	13.07	43.2	25.1	31.7
		-	20	6.6	11.89	26.15	31.6	11.4	57.0
		-	40	6.6	11.89	52.4	41.2	6.1	52.7
Glacial	Scarlet Base RG	50	25	6.6	11.89	32.69	51.7	8.6	39.7
		75	25	6.6	11.89	32.69	57.0	16.5	26.5
		100	25	6.6	11.89	32.69	61.1	22.1	16.8
	Salt of Naphthanil Blue BT	50	25	6.6	11.89	32.69	27.6	8.5	63.9
		75	25	6.6	11.89	32.69	46.1	9.1	44.8
		100	25	6.6	11.89	32.69	55.7	8.3	36.0
Reactive	Helaktyn Yellow D5GN	50	25	6.6	11.89	32.69	53.5	8.3	38.2
		75	25	6.6	11.89	32.69	69.1	7.4	23.5
		100	25	6.6	11.89	32.69	76.0	9.4	14.6

Table 9-9. Effectiveness of ozone oxidation of biologically treated wastewater with the addition of individual dyes of different concentrations

Group of dye	Name of dye	Concentration of dye, mg/l	Contact time, min	Ozone utilized by the sample, mg	Amount of ozone introduced, mg O_3/mg of dye	Amount of ozone utilized, mg O_3/mg of dye	Color removal, %	Color threshold	Dichromate COD, mg O_2/l	Dichromate COD removal, %
-	Biologically treated wastewater without the addition of dye	-	-	-	-	-	-	9.0/100	98.0	-
		-	5	2.22	-	-	0.0	9.0/100	46.0	53.0
		-	10	5.57	-	-	3.5	12.0/100	44.0	55.1
		-	20	8.45	-	-	4.2	19.0/100	40.0	58.1
		-	40	20.83	-	-	0.0	18.0/100	34.0	65.3
Glacial	Scarlet Base RG	50	-	-	-	-	-	1.0/100	72.6	-
		50	25	16.93	0.871	0.451	45.1	5.2/100	65.3	10.0
		75	-	-	-	-	-	1.0/100	76.3	-
		75	25	18.65	0.581	0.331	44.3	4.5/100	49.0	35.8
		100	-	-	-	-	-	0.5/100	94.5	-
		100	25	19.97	0.436	0.266	26.5	1.75/100	70.8	25.3
	Salt of Naphthanil Blue BT	50	-	-	-	-	-	1.0/100	64.9	-
		50	25	17.51	0.871	0.467	80.3	3.0/100	52.7	18.8
		75	-	-	-	-	-	0.52/100	86.0	-
		75	25	22.58	0.581	0.401	63.3	1.26/100	70.2	18.4
		100	-	-	-	-	-	0.32/100	98.2	-
		100	25	24.83	0.436	0.331	55.1	0.75/100	77.3	21.3
Reactive	Helaktyn Yellow D5GN	50	-	-	-	-	-	0.70/100	69.0	-
		50	25	9.02	0.871	0.241	71.2	10.0/100	65.3	5.4
Reactive (con.)	Helaktyn Yellow D5GN (con.)	75	-	-	-	-	-	0.50/100	74.5	-
		75	25	15.08	0.581	0.268	60.5	5.0/100	70.2	5.8
		100	-	-	-	-	-	0.37/100	84.2	-
		100	25	18.23	0.436	0.243	51.9	3.1/100	64.9	23.0

Table 9-10. Continuous cocurrent ozonation on a laboratory scale of biologically treated and filtered wastewater--ozone balance and contaminant removal

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Time of process, min	Ozone balance, %			pH		Color threshold		Color--average light absorption, E		
				Used and decomposed in column	In effluent leaving column	In exit gas	Before	After	Before	After	Before	After	Removal, %
1	10.0	55.0	20	63.9	3.7	32.4	8.3	7.75	12/100	26/100	0.227	0.118	48.0
			40	61.8	4.2	33.8	8.3	7.7	12/100	24/100	0.227	0.116	48.9
			60	59.2	3.5	37.3	8.3	7.8	12/100	24/100	0.227	0.124	45.3
			80	59.4	3.3	37.3	8.3	7.8	12/100	24/100	0.227	0.112	50.6
	Average data in test no. 1			61.1	3.7	35.2					0.227	0.117	48.4
2	20.3	55.0	40	56.3	3.0	40.7	8.3	7.65	12/100	30/100	0.227	0.097	57.2
			80	56.7	3.3	40.0	8.3	7.65	12/100	28/100	0.227	0.109	52.0
			120	52.9	3.7	43.4	8.3	7.65	12/100	30/100	0.227	0.091	59.9
			160	54.7	3.7	41.6	8.3	7.7	12/100	30/100	0.227	0.098	56.8
	Average data in test no. 2			55.2	3.4	41.4					0.227	0.098	36.8
3	21.3	55.0	30	34.4	4.5	61.1	8.0	7.6	5/100	23/100	0.416	0.253	39.2
			60	40.8	5.2	54.0	8.0	7.7	5/100	22/100	0.416	0.246	40.9
			90	67.3	4.0	28.7	8.0	7.7	5/100	21/100	0.416	0.221	46.9
			120	46.0	4.9	49.1	8.0	7.7	5/100	22/100	0.416	0.295	29.1
			150	53.8	3.8	42.4	8.0	7.7	5/100	21/100	0.416	0.241	42.1
	Average data in test no. 3			48.5	4.5	47.0					0.416	0.251	39.7

Table 9-10 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Time of process, min	Ozone balance, %			pH		Color threshold		Color--average light absorption, E		
				Used and decomposed in column	In effluent leaving column	In exit gas	Before	After	Before	After	Before	After	Removal, %
4	21.3	55.0	30	69.6	3.6	26.8	8.0	7.9	5/100	20/100	0.416	0.252	39.4
			60	72.1	2.9	25.0	8.0	7.95	5/100	22/100	0.416	0.259	37.8
			90	53.3	3.2	43.5	8.0	8.0	5/100	20/100	0.416	0.233	44.0
			120	56.8	4.3	38.9	8.0	7.95	5/100	20/100	0.416	0.257	38.2
			150	59.6	5.2	35.2	8.0	7.95	5/100	19/100	0.416	0.229	45.0
	Average data in test no. 4			62.3	3.8	33.9					0.416	0.246	40.8
5	21.3	134.7	30	65.5	1.5	33.0	8.0	8.0	5/100	22/100	0.416	0.207	50.3
			60	65.5	2.3	32.2	8.0	7.85	5/100	22/100	0.416	0.255	39.7
			90	65.2	1.8	32.6	8.0	7.9	5/100	23/100	0.416	0.223	46.3
			120	65.0	2.0	33.0	8.0	7.95	5/100	23/100	0.416	0.203	51.2
	Average data in test no. 5			65.4	1.9	32.7					0.416	0.222	46.6
6	30.0	77.7	60	51.1	4.5	44.0	8.0	7.7	5/100	25/100	0.416	0.164	60.6
			120	48.3	3.5	48.2	8.0	7.6	5/100	27/100	0.416	0.169	59.3
			180	51.9	3.7	44.4	8.0	7.75	5/100	27/100	0.416	0.157	62.3
			240	49.6	4.1	46.3	8.0	7.65	5/100	26/100	0.416	0.147	54.7
	Average data in test no. 6			50.4	3.9	45.7					0.416	0.159	61.7
7	32.0	55.0	60	71.7	4.5	23.8	8.3	7.75	12/100	32/100	0.227	0.126	57.3
			120	65.6	5.1	29.3	8.3	8.2	12/100	32/100	0.227	0.114	49.8
			180	72.6	3.6	23.8	8.3	7.9	12/100	32/100	0.227	0.105	53.7
			240	71.3	3.6	25.1	8.3	8.05	12/100	31/100	0.227	0.110	51.5
	Average data in test no. 7			70.3	4.2	25.5					0.227	0.113	50.2

Table 9-10 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Time of process, min	Dichromate COD			Anionic detergents			Nonionic detergents		
				Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
1	10.0	55.0	20	146.8	97.9	33.3	0.56	0.12	78.6	8.30	3.95	52.5
			40	146.8	126.4	13.9	0.56	0.18	67.8	8.30	5.20	37.4
			60	146.8	126.4	13.9	0.56	0.11	80.3	8.30	4.25	48.8
			80	146.8	118.3	19.4	0.56	0.11	80.3	8.30	4.20	49.4
	Average data in test no. 1			146.8	117.2	20.1	0.56	0.13	76.8	8.30	4.10	50.6
2	20.3	55.0	40	146.8	89.8	38.8	0.56	0.11	80.3	8.30	3.25	60.9
			80	146.8	89.8	38.8	0.56	0.13	76.7	8.30	4.50	45.8
			120	146.8	97.9	33.3	0.56	0.13	76.7	8.30	3.55	57.2
			160	146.8	85.6	41.6	0.56	0.13	76.7	8.30	4.15	50.0
	Average data in test no. 2			146.8	90.7	38.2	0.56	0.12	78.6	8.30	3.86	53.5
3	21.3	55.0	30	220.0	164.0	25.4	1.41	0.55	61.0	15.30	6.70	56.2
			60	220.0	156.0	29.1	1.41	0.81	42.6	15.30	7.50	51.0
			90	220.0	144.0	34.5	1.41	0.75	46.8	15.30	7.30	52.3
			120	220.0	146.0	33.6	1.41	0.67	52.5	15.30	7.20	52.0
			150	220.0	160.0	27.3	1.41	0.81	42.6	15.30	7.30	52.3
	Average data in test no. 3			220.0	154.0	30.0	1.41	0.71	49.6	15.30	7.20	52.9
4	21.3	55.0	30	220.0	180.0	18.2	1.41	0.84	40.4	15.30	7.70	49.7
			60	220.0	176.0	20.0	1.41	1.04	26.3	15.30	8.80	42.5

Table 9-10 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Time of process, min	Dichromate COD			Anionic detergents			Nonionic detergents		
				Before, mg/l	After mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
4 (con.)			90	220.0	168.0	23.6	1.41	1.00	29.1	15.30	8.35	45.5
			120	220.0	188.0	14.5	1.41	0.83	41.1	15.30	7.05	54.0
			150	220.0	180.0	18.2	1.41	1.07	24.1	15.30	7.35	52.0
	Average data in test no. 4			220.0	178.4	18.9	1.41	0.95	32.6	15.30	7.85	48.7
5	21.3	134.7	30	220.0	164.0	25.4	1.41	0.61	56.7	15.30	10.9	28.8
			60	220 0	160.0	27.3	1.41	0.74	47.5	15.30	5.24	66.0
			90	220.0	148.0	32.7	1.41	0.78	44.7	15.30	4.04	73.9
			120	220.0	156.0	29.1	1.41	0.42	70.2	15.30	4.40	71.3
	Average data in test no. 5			220.0	157.0	28.6	1.41	0.63	55.3	15.30	6.14	59.8
6	30.0	77.7	60	220.0	184.0	16.4	1.41	0.40	71.6	15.30	6.75	55.9
			120	220.0	180.0	18.2	1.41	0.42	50.2	15.30	7.15	53.3
			180	220.0	196.0	10.9	1.41	0.39	72.3	15.30	6.75	55.9
			240	220.0	168.0	23.6	1.41	0.32	77.3	15.30	6.35	58.5
	Average data in test no. 6			220.0	182.0	17.2	1.41	0.38	73.0	15.30	6.75	55.9
7	32.0	55.0	60	146.8	126.5	13.8	0.56	0.31	44.6	8.30	2.80	68.3
			120	146.8	97.9	33.3	0.56	0.28	50.0	8.30	3.25	60.9
			180	146.8	102.0	30.5	0.56	0.22	60.7	8.30	3.25	60.9
			240	146.8	102.0	30.5	0.56	0.30	46.4	8.30	3.20	61.5
	Average data in test no. 7			146.8	107.1	27.0	0.56	0.27	51.8	8.30	3.12	62.4

Table 9-11. One-stage continuous countercurrent ozonation of biologically treated and filtered wastewater--ozone balance and color removal

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Ozone balance, %: Used and decomposed in column	Ozone balance, %: In effluent leaving	Ozone balance, %: In exit gas	pH: Before	pH: After	Color threshold: Before	Color threshold: After	Color, mg/l Pt: Before	Color, mg/l Pt: After	Color - average light absorption, E: Before	Color - average light absorption, E: After	Removal %
8		9.9	60.8	2.8	36.4	7.6	7.6	2/100	10/100	pink	100	0.420	0.399	5.0
9		9.9	61.0	2.8	36.2	7.6	7.5	2/100	10/100	pink	100	0.440	0.418	5.0
10		30.6	62.5	2.6	34.9	8.0	8.3	2/100	10/100	pink	80	0.435	0.379	12.8
11		30.6	62.2	3.2	34.6	8.0	8.2	2/100	10/100	pink	80	0.353	0.318	9.9
12		30.6	63.0	2.8	34.2	7.9	7.9	2/100	10/100	pink	80	0.320	0.280	12.5
13	15	49.6	77.6	2.1	20.3	7.8	7.8	5/100	15/100	pink	160	0.230	0.190	17.4
14		49.6	76.0	3.1	20.9	7.6	7.6	5/100	12/100	pink	160	0.255	0.207	18.8
15		49.6	76.5	2.8	20.7	7.6	7.6	5/100	15/100	pink	150	0.250	0.198	20.9
16		69.3	81.0	1.9	17.1	7.7	7.6	5/100	20/100	pink	50	0.252	0.152	39.7
17		69.3	78.2	2.1	19.7	7.7	7.8	4/100	15/100	pink	60	0.266	0.155	41.7
18		69.3	79.3	2.0	18.7	7.7	7.7	5/100	15/100	pink	60	0.250	0.150	10.0
19		9.8	60.7	2.2	37.1	7.7	7.6	2/100	10/100	pink	100	0.423	0.291	31.2
20		9.8	61.3	2.2	36.5	7.7	7.6	2/100	10/100	pink	100	0.410	0.278	32.2
21		29.8	65.3	2.3	32.4	7.5	7.6	12/100	35/100	80	30	0.140	0.078	44.3
22		29.8	64.9	2.3	32.8	7.6	7.5	12/100	35/100	80	30	0.134	0.073	45.5
23		29.8	65.1	2.2	32.7	7.6	7.6	12/100	35/100	80	30	0.138	0.075	45.6
24	30	49.0	62.2	1.7	36.1	7.6	7.7	2/100	25/100	pink	40	0.223	0.105	52.9
25		49.0	61.3	2.3	36.4	7.6	7.8	2/100	20/100	pink	50	0.272	0.135	50.3
26		49.0	61.9	1.9	36.2	7.6	7.7	3/100	20/100	pink	50	0.264	0.128	51.5
27		69.5	61.0	1.7	37.3	7.6	7.5	1/100	15/100	pink	60	0.279	0.125	55.2
28		69.5	60.7	1.6	37.7	7.5	7.6	2/100	15/100	pink	60	0.300	0.130	56.6
29		69.5	60.8	1.6	37.6	7.5	7.6	2/100	15/100	pink	60	0.290	0.130	55.2
30		9.9	62.5	2.8	34.7	7.7	7.7	2/100	10/100	pink	80	0.430	0.295	31.4
31		9.9	62.4	2.7	34.9	7.7	7.6	2/100	10/100	pink	80	0.415	0.281	32.3

Table 9-11 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	Ozone balance, %: Used and decomposed in column	Ozone balance, %: In effluent leaving	Ozone balance, %: In exit gas	pH: Before	pH: After	Color threshold: Before	Color threshold: After	Color, mg/l Pt: Before	Color, mg/l Pt: After	Color - average light absorption, E: Before	Color - average light absorption, E: After	Removal %
32		29.6	65.7	3.7	30.6	6.8	6.8	10/100	50/100	100	20	0.117	0.058	30.4
33		29.6	63.5	3.1	33.4	7.3	7.4	5/100	10/100	200	100	0.372	0.207	41.3
34		29.6	60.9	3.0	36.1	7.2	7.6	2/100	10/100	pink	100	0.378	0.225	40.4
35	40	49.2	61.4	2.6	36.0	7.5	7.4	5/100	15/100	light pink	60	0.331	0.166	49.9
36		49.2	63.4	3.0	33.6	7.2	7.0	4/100	25/100	light pink	40	0.135	0.074	45.2
37		10.2	60.0	3.0	37.0	7.3	7.1	3/100	35/100	light pink	30	0.205	0.100	46.3
38		70.1	64.1	2.2	33.7	7.4	7.1	4/100	15/100	light pink	60	0.268	0.120	55.2
39		70.1	63.2	2.5	34.3	7.4	7.3	2/100	35/100	pink	30	0.227	0.103	51.8
40		70.1	63.0	2.3	34.7	7.8	7.8	3/100	35/100	pink	10	0.259	0.116	55.2
41		9.9	63.5	2.0	34.5	7.5	7.5	2/100	35/100	pink	80	0.380	0.302	20.5
42		9.9	63.5	1.9	34.6	7.5	7.5	2/100	10/100	pink	80	0.350	0.270	20.5
43		29.8	66.8	2.0	31.2	7.4	7.5	1/100	10/100	grey-green	160	0.405	0.275	32.1
44		29.8	66.4	2.1	31.5	7.4	7.4	1/100	5/100	grey-green	160	0.450	0.290	35.5
45	50	29.8	66.5	2.0	31.5	7.4	7.4	1/100	5/100	grey-green	160	0.420	0.270	33.7
46		49.1	63.0	1.6	35.4	7.4	7.3	2/100	5/100	grey-green	100	0.381	0.254	33.3
47		49.1	64.1	1.4	34.5	7.5	7.4	2/100	8/100	grey-green	100	0.445	0.280	37.1
48		49.1	63.7	1.5	34.8	7.5	7.5	2/100	8/100	grey-green	100	0.423	0.270	39.2
49		69.7	61.0	1.5	37.5	7.5	7.7	1/100	8/100	pink	100	0.408	0.235	42.1
50		69.7	61.6	1.3	37.1	7.5	7.6	1/100	8/100	pink	100	0.401	0.295	40.3
51		69.7	61.2	1.4	37.4	7.5	7.6	1/100	8/100	pink	100	0.405	0.210	40.1

Table 9-12. One-stage continuous countercurrent ozonation of biologically treated and filtered wastewater -- BOD_5, COD, and detergent removal

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	BOD_5			Dichromate COD			Permanganate COD			Anionic detergents			Nonionic detergents		
			Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
8	15	9.9	30.5	30.5	0.0	170.3	170.3	0.0	40.5	38.0	6.1	0.50	0.42	16.0	8.5	8.0	5.8
9		9.9	29.0	29.0	0.0	162.8	162.8	0.0	36.0	34.0	5.5	0.53	0.44	16.9	7.3	6.9	5.4
10		30.6	34.0	30.0	11.7	195.4	191.2	2.1	36.4	34.0	6.6	1.14	0.87	31.0	7.3	6.3	13.6
11		30.6	35.0	31.0	11.4	181.0	177.8	1.8	49.6	40.8	17.7	0.90	0.61	32.2	8.2	6.8	17.0
12		30.6	35.0	31.5	10.0	130.3	126.0	3.3	41.3	35.8	13.3	0.94	0.63	33.0	8.3	7.0	15.1
13		49.6	20.0	20.0	0.0	118.4	115.2	2.7	28.8	25.2	12.5	0.47	0.27	42.5	4.6	3.5	24.7
14		49.6	20.0	20.0	0.0	126.4	120.0	5.1	32.4	30.4	6.2	0.44	0.21	52.5	5.7	4.1	27.2
15		49.6	19.0	19.0	0.0	93.8	89.8	4.2	30.7	27.8	9.4	0.43	0.22	48.8	5.8	4.3	25.8
16		69.3	20.0	20.0	0.0	69.1	62.2	10.0	32.0	26.0	18.7	0.48	0.15	68.7	6.9	4.0	42.4
17		69.3	35.0	35.0	0.0	110.4	92.0	16.6	32.0	25.6	20.0	0.48	0.15	68.7	6.7	4.2	37.0
18		69.3	25.0	25.0	0.0	115.8	96.3	16.8	30.9	26.3	14.9	0.49	0.16	67.3	6.8	4.2	38.5
19	30	9.8	25.3	25.3	0.0	160.0	140.0	12.5	46.0	39.6	14.1	0.60	0.42	30.0	9.4	6.6	29.7
20		9.8	24.0	24.0	0.0	158.0	138.1	12.6	48.0	41.5	13.5	0.60	0.43	28.3	8.9	6.2	30.3
21		29.8	16.5	12.5	24.2	160.0	130.2	18.6	14.4	12.0	16.6	0.36	0.21	41.6	8.5	1.9	41.7
22		29.8	10.5	9.0	14.2	124.0	105.7	14.7	25.2	22.8	9.5	0.33	0.19	42.4	6.5	3.9	40.0
23		29.8	12.2	10.0	18.0	112.0	92.3	17.5	22.3	19.2	13.9	0.40	0.23	42.5	7.1	3.8	46.4
24		49.0	15.0	13.5	10.0	96.0	74.0	22.7	14.8	11.2	24.3	0.59	0.22	62.7	16.0	7.1	55.6
25		49.0	17.0	14.0	17.6	112.0	88.0	21.7	26.4	22.4	15.1	0.69	0.27	60.8	18.6	9.1	50.8
26		49.0	17.0	14.5	14.7	118.6	90.0	24.1	27.8	23.5	15.4	0.70	0.27	61.4	18.2	9.0	50.5
27		69.5	15.0	13.0	13.3	120.0	90.0	25.0	30.0	24.4	18.6	0.73	0.16	78.0	17.0	6.3	62.6

Table 9-12 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	BOD$_5$			Dichromate COD			Permanganate COD			Anionic detergents			Nonionic detergents		
			Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
28	40	69.5	20.0	16.0	20.0	135.0	99.4	26.3	35.2	27.2	22.7	0.74	0.16	78.3	28.4	10.9	61.6
29		69.5	18.0	15.0	16.6	130.2	97.5	25.1	34.3	27.0	21.3	0.74	0.17	77.0	28.7	10.4	63.7
30		9.9	31.0	29.5	4.8	130.0	107.8	17.0	35.4	30.0	15.2	0.57	0.37	35.0	12.5	9.2	26.0
31		9.9	30.0	28.5	5.0	125.3	105.1	16.0	40.0	33.5	16.2	0.57	0.36	36.8	15.2	11.7	26.1
32		29.6	9.3	7.7	17.2	137.3	98.8	28.0	15.4	12.8	16.8	0.43	0.20	53.5	7.5	4.8	36.0
33		29.6	22.5	18.0	20.0	162.2	124.7	23.1	28.2	25.3	10.2	0.65	0.32	50.7	12.2	7.6	37.2
34		29.6	25.0	20.0	20.0	157.8	120.7	23.5	38.0	32.5	14.5	0.68	0.31	54.4	12.5	0.1	35.2
35		49.2	20.0	15.0	25.0	144.1	109.0	24.3	40.0	27.5	31.2	0.67	0.20	70.1	15.5	0.0	43.3
36		49.2	16.2	15.0	7.4	93.6	64.0	31.6	21.5	14.0	34.8	0.47	0.15	68.1	5.9	3.1	42.0
37		49.2	16.5	14.1	14.5	89.4	62.4	30.2	23.0	15.0	34.7	0.52	0.18	65.3	0.1	3.2	46.7
38		70.1	14.0	14.0	0.0	87.4	58.0	33.6	31.2	21.2	32.0	0.57	0.06	89.4	9.4	1.0	57.0
39		70.1	14.5	14.5	0.0	90.0	60.8	32.4	32.0	22.4	30.0	0.61	0.12	80.3	8.2	3.3	57.5
40		70.1	15.5	15.5	0.0	88.0	59.7	32.1	25.0	19.2	23.2	0.52	0.06	88.4	9.0	3.5	56.2
41		9.8	15.0	14.2	5.3	98.0	88.2	10.0	25.0	22.5	10.0	0.59	0.14	25.4	11.6	9.9	15.0
42		9.8	20.0	19.2	4.0	110.2	99.2	9.9	30.8	27.5	10.7	0.57	0.42	26.3	10.0	8.5	15.0
43		29.8	36.0	35.0	2.7	195.8	153.6	21.5	46.0	38.0	17.4	0.50	0.30	40.0	14.2	10.3	26.0
44		29.8	50.0	41.0	18.0	165.1	138.2	16.2	48.0	36.2	24.5	0.56	0.33	41.0	11.9	9.6	27.7
45	50	29.8	46.0	35.0	24.0	170.0	139.3	18.0	48.6	37.3	23.2	0.58	0.33	43.1	11.6	8.5	28.4
46		49.1	45.0	44.0	2.2	199.6	145.9	26.9	51.6	37.2	27.9	0.63	0.32	49.2	10.0	6.0	37.6
47		49.1	50.0	43.0	14.0	201.2	149.8	25.5	52.8	40.8	22.7	0.57	0.26	54.3	13.0	9.0	43.6

Table 9-12 (con.)

Test no.	Detention time in column, min	Ozone conc. in wastewater in column, mg/l	BOD$_5$			Dichromate COD			Permanganate COD			Anionic detergents			Nonionic detergents		
			Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
48		49.1	50.0	44.0	12.0	200.8	150.0	25.3	51.8	38.3	26.1	0.57	0.27	52.6	12.7	7.5	40.2
49		69.7	28.5	28.5	0.0	147.2	103.0	30.0	45.0	32.4	28.0	0.56	0.20	64.2	14.7	7.2	51.0
50		69.7	34.5	34.5	0.0	139.8	95.0	32.0	50.0	36.2	27.6	0.47	0.16	65.9	14.2	7.0	50.0
51		69.7	32.0	32.0	0.0	141.3	96.2	31.9	49.2	37.0	24.8	0.49	0.17	65.3	14.5	7.0	51.0

Table 9-13. Double-stage continuous ozonation of biologically treated and filtered wastewater--ozone balance and color removal

Test no.	Contact time in column, min.	Ozone conc. in waste-water in column, mg/l	Ozone balance, %			pH		Color threshold		Color, mg/l pt		Color - average light absorption, E		
			Used and decomposed in column	In effluent leaving column	In exit gas	Before	After	Before	After	Before	After	Before	After	Removal, %
52	15	10.0	58.2	4.6	37.2	7.8	7.8	1/100	15/100	pink	60	0.357	0.196	45.1
53		10.0	54.6	4.9	40.5	7.8	7.7	1/100	15/100	pink	60	0.401	0.210	47.6
54		30.0	54.8	3.0	42.2	7.7	7.7	0.5/100	15/100	pink	60	0.323	0.140	56.8
55		30.0	56.7	2.8	40.5	8.0	7.9	0.5/100	15/100	pink	60	0.337	0.150	55.5
56		50.8	54.8	2.4	42.8	7.8	7.7	1/100	15/100	pink	60	0.404	0.163	59.6
57		50.8	55.2	2.3	42.5	7.8	7.7	1/100	15/100	pink	60	0.420	0.170	59.5
58		70.6	60.3	2.6	37.1	7.7	7.6	1/100	15/100	pink	60	0.436	0.155	64.4
59		70.6	61.0	2.2	36.8	7.7	7.7	1/100	15/100	pink	60	0.430	0.152	64.6
60	30	9.6	68.3	4.5	27.2	7.7	7.8	0.5/100	2/100	pink	light pink	0.322	0.175	45.6
61		9.6	71.8	6.0	22.2	7.7	7.6	2/100	10/100	grey-green	100	0.290	0.155	49.5
62		29.8	60.0	2.9	37.1	7.5	7.6	1/100	2/100	pink	200	0.482	0.220	54.3
63		29.8	52.3	3.5	44.2	7.2	7.4	1/100	3/100	pink	150	0.457	0.210	54.0
64		50.4	54.4	2.2	43.4	7.3	7.4	1/100	8/100	pink	100	0.409	0.160	60.8
65		50.4	53.1	2.2	44.7	7.7	7.9	1/100	10/100	pink	80	0.365	0.150	58.9
66		69.4	54.7	1.7	43.6	7.8	7.8	1/100	8/100	pink	100	0.332	0.115	65.3
67		69.4	60.4	1.6	38.0	7.8	7.9	0.5/100	15/100	pink	60	0.371	0.135	69.6
68	50	9.7	52.7	5.0	42.3	7.6	7.7	1/100	10/100	grey-black	100	0.351	0.180	48.7
69		9.7	57.6	5.3	37.1	7.8	7.9	1/100	10/100	grey-black	100	0.408	0.223	45.3
70		30.0	59.6	3.6	36.8	7.4	7.3	8/100	20/100	120	50	0.210	0.092	56.2
71		30.0	55.5	3.4	41.1	7.6	7.6	5/100	15/100	160	60	0.236	0.102	56.8
72		50.1	58.1	2.7	39.2	7.6	7.6	2/100	15/100	pink	60	0.223	0.089	60.1
73		50.1	59.4	2.3	35.0	7.7	7.7	2.100	15/100	pink	60	0.281	0.112	60.1
74		69.6	62.0	1.7	36.3	7.6	7.6	2/100	15/100	pink	60	0.293	0.096	67.2
75		69.6	62.8	1.2	36.0	7.7	7.6	1/100	15/100	pink	60	0.294	0.096	67.3

Table 9-14. Double-stage continuous ozonation of biologically treated and filtered wastewater -- BOD_5, COD, and detergent removal

			BOD_5			Dichromate COD			Permanganate COD			Anionic detergents			Nonionic detergents		
Test no.	Contact time in column, min	Ozone conc. in wastewater in column, mg/l	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
52	15	10.0	27.0	23.0	14.8	104.2	94.1	9.7	60.0	52.0	20.0	0.58	0.28	51.7	14.7	10.6	23.9
53		10.0	20.0	20.0	0.0	114.2	102.5	10.2	64.0	51.0	20.3	0.61	0.32	47.5	17.0	13.0	23.6
54		30.0	16.5	16.5	0.0	91.5	79.8	12.7	60.0	48.0	20.0	0.42	0.13	69.0	11.4	9.3	33.3
55		30.0	23.0	23.0	0.0	130.2	113.0	13.2	63.0	48.0	22.2	0.59	0.19	67.8	21.0	13.0	37.6
56		50.8	45.0	32.0	28.8	133.8	105.6	21.0	68.0	54.0	20.6	0.75	0.10	86.6	18.6	10.4	44.1
57		50.8	40.0	37.0	7.5	125.2	98.0	21.7	72.3	58.2	19.5	0.72	0.12	83.3	19.3	11.2	41.9
58		70.6	37.5	37.5	0.0	197.1	144.3	26.7	84.0	68.0	19.0	0.68	0.10	85.3	23.8	9.7	51.2
59		70.6	37.0	37.0	0.0	200.8	145.0	27.8	84.5	67.0	20.8	0.70	0.08	83.5	22.5	10.2	52.0
60	30	9.6	31.0	31.0	0.0	201.0	175.0	12.9	33.2	28.0	15.6	0.41	0.20	51.2	31.6	22.00	30.3
61		9.6	30.0	30.0	0.0	107.5	92.0	14.4	41.0	34.3	16.3	0.50	0.25	50.0	15.0	18.60	29.3
62		29.8	72.0	66.0	8.3	205.0	175.4	14.4	28.0	21.0	25.0	0.89	0.32	68.5	31.6	20.60	34.9
63		29.8	45.0	44.0	2.2	280.0	242.0	16.2	26.4	20.0	24.2	0.75	0.23	69.3	10.9	6.65	39.0
64		50.4	39.0	35.0	10.2	208.2	168.5	19.3	42.5	33.0	22.3	0.59	0.10	83.0	6.75	3.30	51.1
65		50.4	31.0	29.0	6.4	170.4	135.0	20.7	34.0	26.0	23.5	0.55	0.09	83.6	11.0	5.00	54.5
66		69.4	30.5	29.0	4.9	177.2	130.0	26.6	34.5	26.5	23.1	0.62	0.09	85.4	11.6	4.75	59.0
67		69.4	28.0	27.0	3.6	132.9	98.0	26.2	26.0	20.0	23.0	0.42	0.06	85.7	12.7	5.25	58.6
68	50	9.7	18.0	17.0	5.5	107.5	87.4	18.7	30.8	25.6	16.9	0.75	0.37	50.6	17.0	9.20	45.8
69		9.7	17.0	17.0	0.0	107.5	87.0	19.0	29.0	24.0	17.2	0.70	0.34	51.4	16.0	9.05	45.4
70		30.0	15.0	14.0	6.6	126.7	105.1	17.1	22.0	16.0	27.2	0.63	0.19	69.8	12.7	6.00	58.7
71		30.0	14.5	14.5	0.0	91.5	74.5	18.5	42.0	30.8	26.6	0.59	0.18	69.5	12.2	7.00	44.8
72		50.1	19.5	19.0	2.5	91.5	73.4	19.8	48.0	34.0	29.1	0.35	0.06	82.8	10.6	5.70	46.2
73		50.1	14.5	14.0	3.4	105.6	83.9	20.5	58.0	40.0	30.0	0.56	0.08	82.6	9.7	3.95	59.2
74		69.6	16.0	16.0	0.0	91.8	67.0	27.0	36.0	22.5	29.4	0.42	0.06	85.7	14.5	5.60	61.4
75		69.6	17.5	17.0	2.8	114.4	83.0	27.4	22.5	16.0	28.8	0.40	0.06	85.0	14.5	5.75	60.3

Table 9-15. Comparative table of average values of percentage contaminant removal obtained by single-stage and double-stage ozonation

Contact time, min.	Ozone Conc. in waste-water in column, mg/l	Color - average light, absorption, %		Dichromate COD, %		Anionic detergents, %		Nonionic, detergents %	
		One-stage ozonation	Double-stage ozonation	One-stage ozonation	Double-stage ozonation	One-stage ozonation	Double-stage ozonation	One-stage ozonation	Double-stage ozonation
15	10	5.0	46.3	0.0	10.0	16.0	49.6	5.4	25.7
	30	11.7	56.1	2.4	12.9	32.0	68.4	15.2	35.4
	50	19.0	59.6	4.0	21.3	47.8	84.9	25.9	43.0
	70	40.4	64.4	14.4	27.2	68.2	86.9	39.3	53.1
30	10	31.5	45.8	12.5	13.7	29.0	50.6	30.0	29.8
	30	45.1	54.1	16.9	15.3	42.1	68.9	42.7	36.9
	50	51.5	59.8	22.8	20.0	61.6	83.3	52.3	45.5
	70	55.6	64.4	25.4	26.4	77.7	86.0	62.6	58.8
50	10	20.4	47.0	10.0	18.8	25.3	51.0	15.0	44.6
	30	34.4	56.5	18.5	17.8	41.3	69.6	27.3	51.7
	50	35.5	60.1	25.9	20.1	52.0	82.7	40.7	60.0
	70	46.6	67.3	31.3	27.2	65.1	85.3	50.9	60.8

Table 9-16. One-stage continuous ozonation of biologically treated wastewater after coagulation, filtration, and carbon adsorption processes--ozone balance and color removal

Test no.	Contact time in column, min	Ozone conc. in waste-water in column, mg/l	Ozone balance, %			pH		Color Threshold		Color, mg/l Pt		Color - average light absorption E		
			Used and decomposed in column	In effluent leaving column	In exit gas	Before	After	Before	After	Before	After	Before	After	Removal %
76	30	10.0	42	19	39	7.3	7.3	100/100	60/100	5	15	0.018	0.013	27.7
77		10.0	38	22	40	7.7	7.7	100/100	60/100	5	15	0.018	0.014	22.2
78		10.0	25	35	40	7.1	7.2	100/100	100/100	5	5	0.019	0.014	26.3
79		10.0	25	34	41	8.0	8.0	100/100	100/100	5	5	0.014	0.008	42.8
80		10.0	36	27	37	7.2	7.3	100/100	100/100	5	5	0.024	0.010	58.3
81		10.0	44	17	39	7.9	8.0	100/100	100/100	10	10	0.044	0.015	61.3
82		5.0	46	8	46	8.0	8.0	100/100	100/100	5	5	0.057	0.055	3.5
83		5.0	42	10	48	7.8	7.8	65/100	65/100	15	15	0.047	0.036	21.7
84		5.0	40	12	48	7.4	7.5	100/100	100/100	10	10	0.021	0.022	0.0
85		5.0	40	14	46	6.9	6.9	100/100	100/100	10	10	0.005	0.005	0.0
86		5.0	40	13	47	7.3	7.5	100/100	100/100	5	5	0.009	0.006	33.3
87		5.0	32	16	52	7.3	7.4	100/100	100/100	5	5	0.007	0.005	28.6

Table 9-17. One-stage continuous ozonation of biologically treated wastewater after coagulation, filtration, and carbon adsorption processes--BOD_5, COD, TOC, and detergent removal

Test no.	Contact time in column, min	Ozone conc. in wastewater in column, mg/l	BOD_5			Dichromate COD			Permanganate COD			TOC			Anionic detergents			Nonionic detergents		
			Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %	Before, mg/l	After, mg/l	Removal, %
76	30	10.0	1.8	2.7	0.0	10.9	9.3	14.6	2.3	2.1	8.7	7.0	6.6	5.7	0.4	0.3	25.0	3.20	1.96	40.6
77		10.0	1.6	0.7	56.2	5.5	3.1	44.0	1.3	1.0	23.0	4.8	-	-	0.0	0.0	-	4.55	3.55	21.9
78		10.0	-	-	-	1.5	1.5	0.0	0.9	0.9	0.0	5.4	-	-	0.0	0.0	-	3.10	1.95	37.8
79		10.0	1.6	2.1	0.0	1.5	1.5	0.0	0.7	0.3	57.1	4.3	6.7	0.0	0.0	0.0	-	2.0	1.25	37.5
80		10.0	3.1	1.2	61.3	4.2	1.4	66.6	0.3	0.2	33.3	5.4	4.8	11.1	0.6	0.03	50.0	3.45	2.15	37.6
81		10.0	3.2	2.9	9.3	14.3	9.5	33.6	1.1	0.8	27.2	4.5	4.8	0.0	0.0	0.0	-	4.0	2.25	13.7
82		5.0	3.2	2.4	9.3	14.3	10.5	26.5	0.9	0.7	22.2	7.2	16.6	0.0	0.0	0.0	-	1.75	1.0	15.8
83		5.0	2.0	2.0	0.0	10.3	7.5	27.1	2.8	2.3	17.8	5.8	6.3	0.0	0.0	0.0	-	1.75	2.80	41.0
84		5.0	1.5	1.5	0.0	7.5	2.8	16.8	1.5	1.5	0.0	7.3	7.0	4.0	0.0	0.0	-	4.0	2.15	49.2
85		5.0	1.9	2.8	0.0	8.0	7.0	12.5	1.1	0.6	45.4	6.3	4.6	27.0	0.0	0.0	-	2.40	1.68	33.3
86		5.0	1.6	1.5	6.3	7.0	6.0	14.3	0.8	0.4	50.0	3.3	3.3	0.0	0.0	0.0	-	3.55	2.90	12.2
87		5.0	2.0	1.2	40.0	2.0	1.0	50.0	0.3	0.1	66.6	2.5	2.4	4.0	0.0	0.0	-	4.55	2.95	43.0

SECTION 10

ION EXCHANGE

INTRODUCTION

Ion exchange is a process which at present is widely used to make water suitable mainly for industrial and energy purposes. The application of the ion-exchange process to the treatment of wastewater is not widespread due to the high costs and practical difficulties connected with regeneration of the ion exchange medium. An additional difficulty is the choking of the ion-exchange mass with organic material of high molecular weight. For this reason, wastewater supplied to the beds must be previously treated by one of the conventional methods, that is, by biological means or by coagulation, and then filtered through sand filters. This wastewater still contains considerable quantities of ions and inorganic nitrogen and phosphates.

In pilot scale research [68] on the removal of phosphates by ion exchange, 90 percent reduction was obtained. The use of ion exchange when removing ammonia nitrogen also gives very good results, ranging from 93 to 97 percent, depending on the degree of purity of the wastewater supplied to the resin beds.

In wastewater management, ion-exchange resins are also used to recover ions because of their usefulness in industry or because of the hazard they present to the wastewater receiver. The publication [71] on the subject of chromate recovery in a dye factory exemplifies this.

Ion-exchange resins are also used in small scale research into determination of the suitability of ion-exchange processes for removing color from dyehouse waste [71]. Color removal of from 50 to 90 percent was obtained for dyes from the acid, basic, and vat groups. Dispersed dyes were not removed on ion-exchange media.

OBJECTIVES

The investigations on ion exchange were carried out with the aim of increasing the effectiveness of treatment of textile wastewater, previously biologically treated, from the ACP.

In the laboratory investigations, the most effective ion-exchange resins were determined from a dozen or so possible choices. The optimal process parameters for this type of wastewater were also determined.

SCOPE OF INVESTIGATION

The investigations were carried out on two parts industrial wastewater to one part municipal sewage. The preliminary laboratory investigations screened the effectiveness of different cationic and anionic resins. The influence of the wastewater filtration rate through the ion-exchange bed on the reduction of pollutants was studied.

The total capacity in meq/ml and the dye capacity (the amount of dye in mg adsorbed through a volume unit of resin) of the resins studied was determined.

The selected resins were used at Andrychow on the pilot scale. Resins used for the investigations include the strongly acid cation Zeolite 325 and the strongly basic anions Amberlite IRA-401 and Zeolite KMP.

The bed-loading in the ion-exchange process for pilot studies amounted to 6, 12, and 18 BV/h, with the application of a dual cationic-anionic system.

The work of a single, entirely anionic system has also been tested, but its results have proved unsatisfactory.

PROCEDURE OF INVESTIGATION

Description of Installation

The preliminary laboratory experiments were carried out in glass columns 1.6 m high and 3.4 cm in diameter. The average height of the ion bed was 1 m.

The experimental installation, constructed on a pilot scale in the experimental station at Andrychow, consisted of three Plexiglas columns 2 m in height and 12 m in diameter. The first column, filled with sand and anthracite, worked as a filter of wastewater fed to the ion-exchange columns after the biological treatment process. After filtration, the wastewater was fed from above to the column filled with the cation. The bed volume was 11.3 l and the layer was 1 m high. Next, the wastewater was fed to the 20-l desorption tank, where the free carbon dioxide was released. After desorption the wastewater was fed to the 11.3-l column filled with the anion. The schema of the installation is presented in figure 10-1.

Method of Laboratory Screening Studies on Resins

In the experimental laboratory columns, 12 types of resins were studied; the seven anionic and five cationic resins of different functional groups are listed in table 10-1.

Biologically treated wastewater in a natural state and the same wastewater with the addition of different dyes, each of a constant concentration of 50 mg/l, were fed to the columns filled with an ion-exchange bed. Dyes characteristic of each given dye group were chosen, using a wastewater flow rate of 1.5 BV/h. If better removal was required for the given dye, flows of 3.0 and 6.0 BV/h were also used.

The ion-exchange process was carried out up to the time when the resins were exhausted, that is, up to the moment when colored wastewater was obtained at the outflow from the column. With dyes difficult to remove, the increase in the level of COD in the outflow was measured.

Analytical control of the process on the laboratory scale covered pH value; COD; anionic detergents; chlorides, where resins in chloride form were used; color specified by spectrophotometer; and color threshold.

Determination of the Exchange Capacity of the Resins Used

Investigations on the laboratory scale determined the total capacity of the resins, the color capacity of the resins, and the wastewater exchange capacity.

Total Capacity of Resins--

The total capacity was determined for all 12 resins used in the diagnostic investigations. This capacity is a constant value for a given resin and signifies the number of milligram-equivalents (meq) of resin that can be exchanged through a unit of mass or volume of resin in certain defined conditions of reaction. It was determined according to the following equation [12,72]:

$$\text{capacity } \frac{\text{meq}}{\text{ml}} = \text{capacity } \frac{\text{meq}}{\text{g}} \times \text{ density } \frac{\text{g}}{\text{ml}} \times \text{ fraction of solids}$$

where

fraction of solids = weight difference between wet resin and resin dried for 8 h at 110° C, divided by wet resin weight.

The laboratory experiments were carried out on small amounts of resins previously prepared with appropriate regenerants. Method [12,72] was used to determine the cation exchange capacity (CEC) for strongly and weakly acidic resins, to determine the anion exchange capacity (TAEC) for strongly basic resins, and to determine the anion exchange capacity (AEC) for weakly basic resins.

The values given in meq/ml that were obtained for moist resin (table 10-2) are approximate to the catalog values of the firm BDH [74]. The resin exchange capacities determined in this way were used when the right amount of solutions of sodium chloride and hydrochloric acid used in regeneration was determined.

Dye Capacity of Resins--

The dye capacity of the resins was determined by feeding, at a flow rate of 6 BV/h, water solutions of individual dyes with a known constant concentration of 50 mg/l into all the fresh ion-exchange resins under investigation. Dyes that were absorbed best by each particular resin were used.

The process was carried out until the dye appeared in the outflow from the column.

The highest capacity from among the strongly basic anionites was shown by Amberlite IRA-401--42.5 mg of the dye Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106) per milliliter of resin. The highest capacity from the strongly acid group was shown by Zeolite 325--13 mg of dye of the Salt of Naphthanil Blue BT per milliliter of resin. The capacities of the other resins were significantly lower. The values obtained, determined in milligrams of dye per milliliter of resin, are compared in table 10-3. The investigations found that a fresh resin bed has a significantly higher capacity for dyes than one that has undergone successive regenerations.

From the investigations, it was possible to determine the level of absorbency decrease in the resin in the course of operation. Tests were carried out on the resins used in the pilot investigations, Amberlite IRA-401 and Zeolite 325, with the highest color capacity. The bed loading was 6 BV/h. For Amberlite, a dye from the indigosol group, Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106) was used; for Zeolite, a glacial dye, Salt of Naphthanil Blue was used.

The decrease in capacity for the given dye after successive regenerations, expressed according to milligrams of dye per milliliter of resin, is presented in table 10-4.

From the 15 successive bed regenerations carried out, it is possible to state that the greatest decrease in capacity can be seen after the first few regenerations of fresh ion-exchange resins. Beyond that, the capacity decreases uniformly, although at a significantly lower level.

Exchange Capacity for Wastewater--

The investigations were carried out on a laboratory scale in a double system (resin beds 300 ml in volume) on resins installed as in the pilot investigations. The cation Zeolite 325 and the anion Amberlite IRA-401 were used. The process was carried out at a rate of 6 BV/h up to the moment when the anion was used up. At this time the cation, which is used up more quickly, was replaced by another exchange bed of the same cation. The cationic resin in the system acted as an exchanger protecting the anionic resin. The removal level obtained for refractory substances on the cationic resin, in contrast to the anionic resin, was not high.

Mixed municipal and industrial wastewater from the biological treatment plant in Andrychow was used for the experiments. When the exchange capacity of the anion was determined, the result was based exclusively on the wastewater alkalinity converted into calcium carbonate (mg of $CaCO_3$). The results for 12 successive series are presented in table 10-5 and graphically in figure 10-2.

The physicochemical analysis of wastewater fed to the system during the investigations is set out in table 10-6. The wastewater was characterized by the very great variability of concentrations of pollutant indicators such as alkalinity and COD. Hence the load of calcium carbonate fed to the beds in successive series was very different. Nevertheless, a certain decrease in the capacity of anionic resin during exploitation is evident.

Regeneration of Ion-Exchange Resins

The regeneration of resins in both the laboratory and the pilot investigations was carried out according to the following sequence of operation:

1. loosening of the mass with water, and
2. regeneration performed in the case of anionic resins with a 10 percent solution of sodium chloride, in the case of cations with a 4 percent solution of hydrochloric acid.

In the laboratory and pilot investigations the regeneration was carried out at a rate of about 3 BV/h. The volume of the regenerative solution was determined according to the exchange capacity of the particular resin on the basis of the formula [72]:

$$\text{volume of regenerative solution (in units of bed volume)} = \frac{\text{exchange capacity of resin (meq/ml)} \times \text{required amount of regenerative solution (meq/ml)}}{\text{normality of regenerative solution (meq/ml)}}$$

The required amount of regenerator is determined from table 10-7 [72]. The exchange capacity values of the resins, expressed in meq/ml of resin, required for calculation were determined in the laboratory separately for each studied resin.

After regeneration, washing was performed for anions until the reaction of the chloride ions ceased, and for cations until acidity decreased to a value of 1 meq/l. The volume of the water used in washing was 10 to 15 BV for anions and 6 to 8 BV for cations.

In the dual cationic-anionic system used in the pilot investigations, the exchange process was carried out up to the time when the cation was exhausted; at this time there was still a certain residual exchange capacity of the anionic resin. Generally, there were about 1.3 regenerations of cation for every one regeneration of anion.

Method of Investigation on the Pilot Scale

The resins selected in the laboratory as having the highest total and dye capacity were used for the investigations:

1. strongly basic Amberlite IRA-401,
2. strongly basic Zeolite KMP, and
3. strongly acid Zeolite 325.

In the first sequence, investigations were carried out exclusively in the single system on an Amberlite IRA-401 anion bed, with a flow rate of 6 BV/h. Three series of investigations were carried out (no. 1, 2, and 3). The results obtained were not satisfactory due to the low reduction of pollutants (tables 10-8, 10-9, and 10-10) and the short work time of the bed. In the further sequence, a cation exchanger was included first in the system to fulfill a protective function for the anion bed, mainly by removing carbon dioxide and hardness.

The ion-exchange process was carried out with a bed loading of 6.12 and 18 BV/h in the double cationic-anionic system. Two systems were used: Zeolite 325-Amberlite IRA-401 and Zeolite 325-Zeolite KMP. Analytical control of work was exercised once every 4 h with a bed loading of 6 BV/h, once every hour with a loading of 12 BV/h, and once every hour or 40 min with a bed loading of 18 BV/h.

The physicochemical analyses were increased relative to the laboratory scale to include pH value, alkalinity, acidity, permanganate COD, BOD_5, dichromate COD, chlorides, anionic detergents, nonionic detergents by the phosphotungstic acid method with hydroquinone modification, color according to the Pt scale, color threshold, and spectrophotometrical color.

Samples of wastewater for physicochemical analyses were collected at the following points:

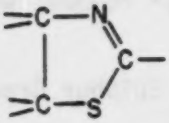
1. biologically treated wastewater, after sand-anthracite filtration but before cation;
2. wastewater in the outflow from the cation column; and
3. wastewater in the outflow from the anion column.

The process was carried out up to the moment the bed was worn out, i.e., up to the time the acidity of wastewater in the outflow from the cation column fell to zero. The work time of the ion-exchange unit and the amount of treated wastewater according to the bed loading for the individual cycles are shown in tables 10-11 through 10-16.

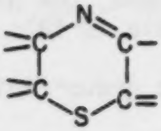
LABORATORY STUDIES ON THE CHARACTERISTICS AND CHOICE OF RESINS

To determine the suitability of resins in removing detergent, color, and other refractory compounds from biologically treated wastewater, a thorough laboratory study was made of 12 types of resin, seven anionic and five cationic resins, from different functional groups. The investigations were carried out on wastewater from the ACP combined with municipal wastewater after biological treatment and filtration without the addition of dyes, and on wastewater to which dyes with concentrations of 50 mg/l had been added.

In the laboratory investigations, a basic bed loading equal to 1.5 BV/h was used. The loadings 3.0 and 6.0 BV/h were used only for dyes subject to good absorption. For the additional coloring of wastewater samples in the laboratory experiments, dyes from the sulfuric, glacial, dispersed, reactive, vat, and indigosol groups were used. From the group of sulfuric dyes, Sulphur Black WT (C.I. Solubilised Sulphur Black 1; 53186) and Sulphur Khaki G (C.I. Sulphur Green 8:1) were used. Dyes of this group are products of the sulfurization of organic compounds and contain characteristic groupings:



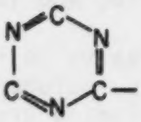
thiazole group



thiazine group

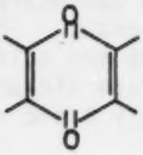
These dyes are insoluble in water. However, when reduced in a solution of sodium sulfide they are transformed into a soluble form.

From the group of glacial dyes the Salt of Naphthanil Blue BT was used. This is one of the azodyes formed on a filament. From the group of sedimentary dyes, Syntene Rubine P-3B (C.I. Disperse Red 5; 11215), Syntene Azure PBGL, Syntene Navy Blue P-BL, and Indanthren Bordeaux RR (C.I. Vat Red 15; 71100) were used to color the wastewater. Reactive dyes were also used: Helaktyn Yellow D-5GN, Helaktyn Yellow DGR, and Drimarene Green X-2BL (C.I. Reactive Green 15). The characteristic grouping of these dyes is:



1, 3, 5 - triazine.

From the group of vat dyes Helanthrene Green BS and Helanthrene Green BT were used. These dyes have the basic quinonoid system:



Indigosol Helasol Grey BL (C.I. Solubilised Vat Black 1; 73671) and Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106) are leukoesters of vat dyes and have hydroxyl groups esterified with sulfuric acid:

$$\equiv C - O - SO_3Na \ .$$

The susceptibility of the chosen dyes from individual dye groups to the ion-exchange process, as well as the usefulness of the resins, was determined. It was found that the most effective resins in the ion-exchange process, because of high total capacity and color capacity, are the anionic resins Amberlite IRA-401 and Zeolite KMP, and the cationic resin Zeolite 325.

The ion-exchange resin Amberlite IRA-401 removed the following dyes well (table 10-17):

- from the sulfuric group--Sulphur Khaki G (C.I. Sulphur Green 8:1), 64 percent;
- from the glacial group--Salt of Naphthanil Blue BT, 91 percent;
- from the reactive group--Helaktyn Yellow D-5GN, 95 percent; Helaktyn Yellow DG-R, 97 percent; Drimarene Green X-2BL (C.I. Reactive Green 15), 63 percent; and
- from the indigosol group--Helasol Grey BL (C.I. Solubilised Vat Black 1; 73671), 83 percent; and Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106), 92 percent.

When Zeolite 325 was used, the highest level of color removal was noted for the following dyes (table 10-18):

- from the sulfuric group--Sulphur Khaki G (C.I. Sulphur Green 8:1), 52 percent;
- from the glacial group--the Salt of Naphthanil Blue BT, 96 percent; and
- from the indigosol group--Helasol Yellow GOK (C.I. Solubilised Vat Yellow 4; 59106), 43 percent.

Helaktyn Yellow D-5GN from the reactive group of dyes did not undergo decolorization (table 10-18).

The best color removal effect for biologically treated wastewater without dyes added, up to 75.2 percent, appeared at the lowest flow rate through the bed, equal to 1.5 BV/h (tables 10-17, 10-18, and 10-19).

The good interaction of some dyes with resins is related to their chemical structure. In the sulfuric dye group, Sulphur Khaki G (C.I. Sulphur Green 8:1) is a dye which has active arylamino groups as well as nitrogen and sulfur atoms linked in a heterocyclic system, and can be linked with both strongly basic and strongly acid resins. Similarly, the Salt of Naphthanil Blue BT contains primary and secondary amino groups attached to the benzene ring, and also the methoxy group. These groups interact with resins. The dyes of the reactive group are sulfonates and link well with strongly basic resins. Indigosols are linked through oxygen atoms to quaternary nitrogen, present in strongly basic resins [71].

The highest level of COD removal was obtained on strongly basic resins: Amberlite IRA-400, 401, and 410, and Zeolite KMP and FFIP. At two different rates, 1.5 and 3.0 BV/h, the results were comparable. The average removal of COD was close to 50 percent (table 10-20).

Significantly worse effects were obtained for weakly basic resins and for strongly and weakly acid resins. The average percentage of COD removal for 1.5 BV/h in this case was from 15 to 45. The removal level of anionic detergents was, in general, highest for strongly basic resins--from 72.9 to 99 percent. Very low detergent removal was achieved with weakly and strongly acid resins (table 10-21).

On the basis of these results, the following resins were selected for investigations on the pilot plant scale:

- strongly basic resin Amberlite IRA-401,
- strongly basic resin Zeolite KMP, and
- strongly acid resin Zeolite 325.

COMMENT ON THE RESULTS OF TECHNOLOGICAL INVESTIGATIONS

On the basis of the laboratory results, pilot investigations were carried out on a half technical scale in the experimental station in Andrychow. A comparison is presented in table 10-22 of the average percentages of pollutant removal obtained in the ion-exchange process in the dual cation Zeolite 325-anion Amberlite IRA-401 system and in the single anion Amberlite IRA-401 system using a bed loading of 6 BV/h. The comparison shows that a dual ion exchange system considerably improves the level of wastewater treatment purification. In further investigations the ion-exchange process was carried out exclusively in a dual cationic-anionic system.

Twenty-five series of investigations were carried out with the anionic resin changed from Amberlite IRA-401 to Zeolite KMP.

1. For series 4 to 8, the pH value after the process varied from 2.1 to 2.6, the acidity from 2.4 to 7.6 meq/l, and the chloride concentration in the outflow from the anion column from 178.0 to 225.0 mg/l.
2. For series 9 to 13, the pH value after the process varied from 2.4 to 2.7, the acidity from 3.4 to 8.4 meq/l, and the chloride concentration from 205.9 to 298.2 mg/l.
3. For series 14 to 16, the pH value after the process varied from 2.0 to 2.3, the acidity from 6.7 to 10.0 meq/l, and the chloride concentration from 258.3 to 418.9. Similar values were obtained when the anionic resin was changed from Amberlite IRA-401 to Zeolite KMP.
4. For series 17 to 19, the pH value after the process fluctuated from 2.3 to 2.4, the acidity from 6.8 to 10.1 meq/l, and the chloride concentration in the outflow from the anion column from 284.0 to 461.5 mg/l.
5. For series 20 to 22, the pH value after the process varied from 2.3 to 2.5, the acidity from 6.1 to 12.2 meq/l, and the chloride concentration from 230.7 to 532.5 mg/l.
6. For series 23 to 25, the pH value after the process varied from 2.3 to 2.6, the acidity from 4.9 to 9.2 meq/l, and the chloride concentration from 230.7 to 376.3 mg/l. The results are given in tables 10-23 to 10-44.

A comparison of the effectiveness of removing average values of permanganate and dichromate COD, BOD_5, anionic and nonionic detergents, color according to the Pt scale, and color determined spectrophotometrically in the ion-exchange process in dual systems is presented in tables 10-45 to 10-50 and graphically in figures 10-3 to 10-6.

A comparison of the average values of pollutant removal for cation Zeolite 325 and the anion Amberlite IRA-401 dual systems at different bed loadings of 6, 12, and 18 BV/h is presented in table 10-51.

The next series of investigations was carried out in the same pilot installation, but the anionic resin Zeolite KMP was used in place of the anion Amberlite IRA-401. The average values of pollutant removal for the cation Zeolite 325 and the anion Zeolite KMP system with a bed loading of 6, 12, and 18 BV/h are shown in table 10-52.

In successive series of investigations, the strong differences in the wastewater used make it impossible to comment upon the influence of hydraulic loading on pollutant removal. The data in table 10-52 show that good results were obtained for removal of color and anionic detergents. Permanganate and dichromate COD were removed to a lesser degree.

DISCUSSION OF THE RESULTS

Investigations on a Laboratory Scale

Resins were chosen for the research conducted in Andrychow by preliminary laboratory tests. Resins with an insufficient or small dye capacity were eliminated. Of the anions examined, Amberlite IRA-401 contained the highest capacity expressed in milligrams of dye--42.5 mg/l--and of the cations, Zeolite 325 contained 13.0 mg/l. For these resins the amount of treated wastewater containing artificially supplied dyes in a concentration of 50 mg/l was, on the average, for each cycle of work: Amberlite IRA-401--26 BV, and Zeolite 325--10 BV.

There are no data regarding the removal of dyes solely by the ion-exchange method. The one publication available to us [71] refers to very small-scale research into the treatment of dyehouse waste in chromatographic columns. In this paper, susceptibility to removal on resins was determined for dyes from different groups: acid, alkaline, vat, and dispersed. It was found that dyes from all these groups, with the exception of the dispersed group, are removed well on resins of different functional groups, in the range of 50 to 96 percent. Total removal of color in the case of dispersed dyes was obtained only on the natural resin XAD-7 preceded in the system by the weakly basic resin Duolite A-7. But when the strongly acid Amberlite IR-120 and weakly acid IRC-50 were used, color removal of only 17 and 30 percent, respectively, was obtained for this group of dyes.

For comparison, in the present investigations the following color removal results were obtained when the same resins, IR-120 and IRC-50, and different process rates were applied:

IR-120: 1.5 BV/h = 10.3%, 3 BV/h = 0.0%
IRC-50: 1.5 BV/h = 37.8%, 3 BV/h = 12%, 6 BV/h = 0.0%.

The results of the investigations for these two resins are, to a large degree, similar.

Investigations on a Pilot Scale

The dual system used in the ion-exchange process consisting of a cation column H^+-Zeolite 325 and an anion column, Cl^--Amberlite IRA-401, or exchangeable Cl^--Zeolite KMP, is appropriate for the treatment of waste with considerable hardness and alkalinity [12,68,74]. In this system the cationic resin, operating as a hydrogen exchanger, also removed free and bound carbon dioxide. This made it possible to avoid additional ion loading of the second, strongly basic resin in the system. The cationic resin also removed color and the remaining pollutants, with the exception of anionic detergents, to a small degree and prolonged the operating time of the system. The average work cycle of the dual system was from 6 to 20 h, depending on the concentration of pollutants in the wastewater supplied. Because of the great variability in the concentrations of pollutants in the wastewater in a particular series of investigations, there is no clear relation between the efficiency of the process defined by the amount of treated waste (expressed in BV) and the loading of the resin beds operating in the dual system.

Taking into account the average values of the investigations (with the use of one type of cationic and two types of anionic resins), the amount of treated wastewater in one work cycle was calculated for the following bed loadings:

6 BV/h: 114 BV,
12 BV/h: 90 BV, and
18 BV/h: 108 BV.

In the investigations quoted in the literature [75], which were carried out on the treatment of biologically treated wastewater by the ion-exchange method using only basic resins in a single system and a loading of 35 and 45 BV/h, the amount of treated wastewater was 200 BV in one work cycle. This high level of efficiency was possible because the wastewater supplied was very pure. From the diagram in this publication [75] it is clear that removal of pollutants, mainly phosphates, was maintained at a constant level only to an efficiency of about 100 BV of wastewater. Then the concentration of pollutants in the wastewater after the ion-exchange process increased considerably.

In another publication [76] dealing with the removal of ammonia nitrogen from biologically treated wastewater on naturally occurring zeolite (clinoptilotite), the average amount of treated waste in a dual system with a bed loading of 6 to 9 BV/h was 232 BV. The ammonia concentration at the inflow was 12 mg/l, at the outflow 1.4 mg/l. On a single bed with the same process rate, the amount of wastewater was 150 BV.

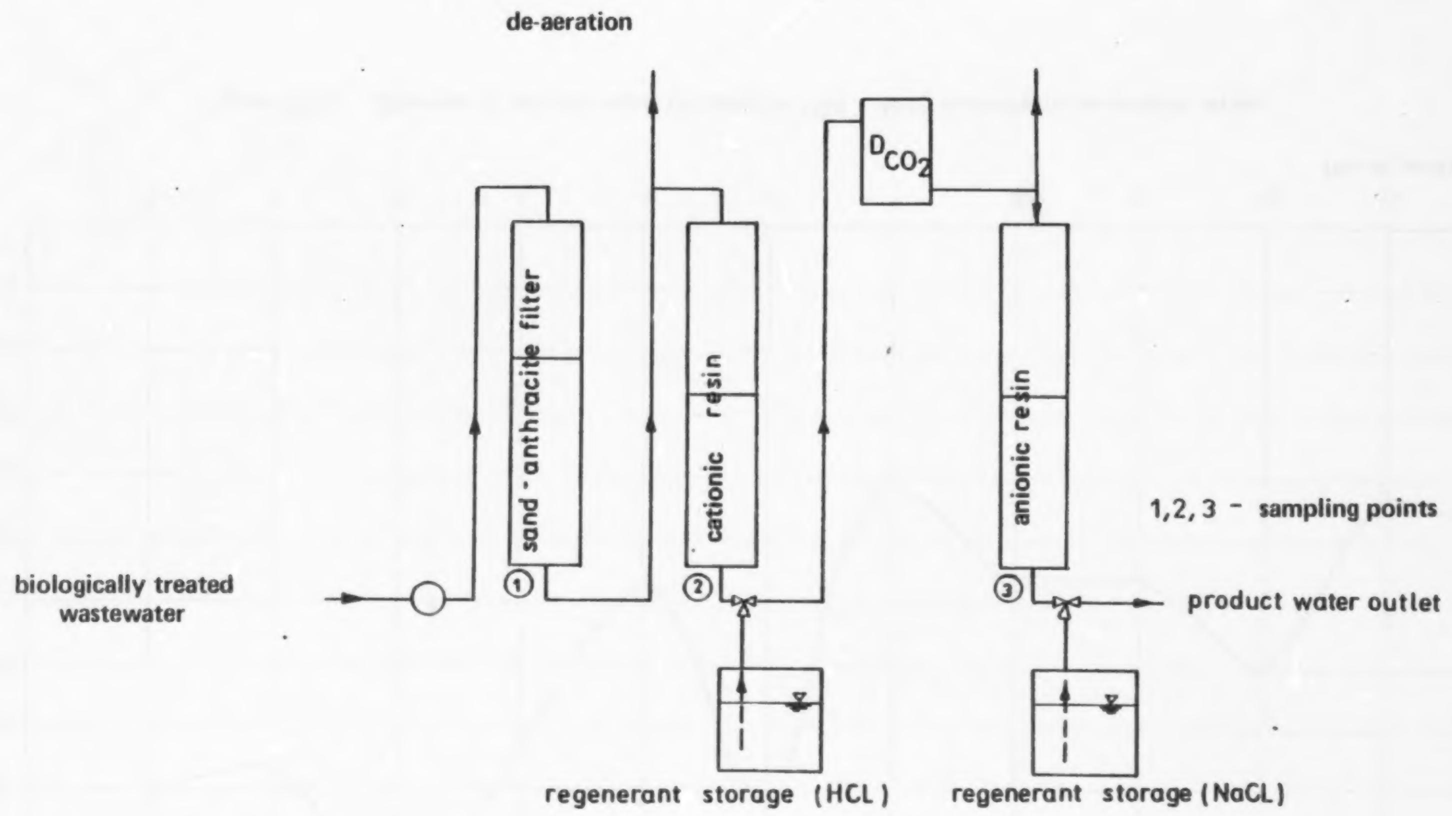
In the previously mentioned laboratory investigations [75] carried out in the second stage of wastewater treatment, nine basic resins in a chloride form were used. The rate of the process was variable--25, 35, and 45 BV/h. The results of removal of such pollutants as alkalinity, phosphates, nitrates, color, total organic carbon, and anionic detergents depended to a large degree on the kind of resin. Very good results were obtained on, among others, Zeolite FFIP and KMP. Color removal was 91.2 and 93.2 percent, respectively. These resins were also used in the present investigations, where it was found that they possess a high dye capacity: for FFIP-22, 6 mg/ml; and for KMP, 17.2 mg/ml.

The degree of color removal obtained in the present investigations was, in comparison with the results mentioned in the literature [75], considerably lower. With a process rate of 6 BV/h it was 30.4 percent for FFIP and 55.4 percent for KMP. The cause of these differences is probably the method of measuring the color. In the research quoted [75], a spectrophotometric measurement of absorption was conducted exclusively for the range of 400 nm. For an objective color determination, a measurement should be made of the light permeability of the sample studied in the range of the visible spectrum, that is, at wavelengths from 400 to 650 nm.

In the case of anionic detergent removal, similar results--about 100 percent removal--were obtained both in the present study and in previous research [75]. Weakly and strongly basic resins possess high sorptive capacity for anionic detergents. The mechanism of this phenomenon is explained in the literature [77].

CONCLUSIONS

1. In the preliminary laboratory investigations to determine the proper types of ion-exchange resins, it was found that strongly basic resins, Amberlite IRA-401 and Zeolite KMP, and a strongly acid resin, Zeolite 325, give the best results for the treatment of textile wastewater.
2. In the pilot plant scale experiments to which the chosen resins were applied, good removal resulted for color, from 74.5 to 87.6 percent, as well as for anionic detergents. Less satisfactory reduction effects, in the range of 58.2 to 96.3 percent, were found for permanganate COD, dichromate COD, and nonionic detergents, which did not exceed 54.1 percent, 46.2 percent, and 58.6 percent, respectively.
3. The effectiveness of the treatment is determined by the use of a dual cationic-anionic system. The cationic resin relieves the anionic bed, extends the removal cycle, and also increases the percentage of pollutant removal.
4. During the regeneration of resins, it was found that the average percentage ratio of regeneration time to work time of the beds was, for a hydraulic bed loading of 6 BV/h, 8.3 to 14.3 percent; for a bed loading of 12 BV/h, 22.2 to 33.3 percent; and for a bed loading of 18 BV/h, 25 to 33.3 percent. The average percentage ratio of volume of postregeneration water to volume of treated water varies from 13.9 to 26.0 percent.
5. After ion exchange, a very low pH, on the average 2 to 3, and a large concentration of chlorides, up to 532 mg/l, were found.
6. In the 12 series of investigations on the exhaustion of resins, a significant decrease was found in the capacity of anionic resin during performance.
7. Disadvantages of the ion-exchange process were found--in particular, the low removal of permanganate COD, dichromate COD, and nonionic detergents; the long regeneration time of the beds in relation to the work time of these beds; the large amount of spent regeneration wastewater; and the low pH and large concentration of chlorides in the treated effluent. These indicate that the ion-exchange process is of little use for the treatment of wastewater from the textile industry. An additional negative factor is the high cost of ion-exchange resins.



de-aeration
biologically treated wastewater
sand - anthracite filter
cationic resin
anionic resin
D_{CO_2}
①
②
③
1,2,3 - sampling points
product water outlet
regenerant storage (HCL)
regenerant storage (NaCL)

Figure 10-1. Scheme of ion-exchange system.

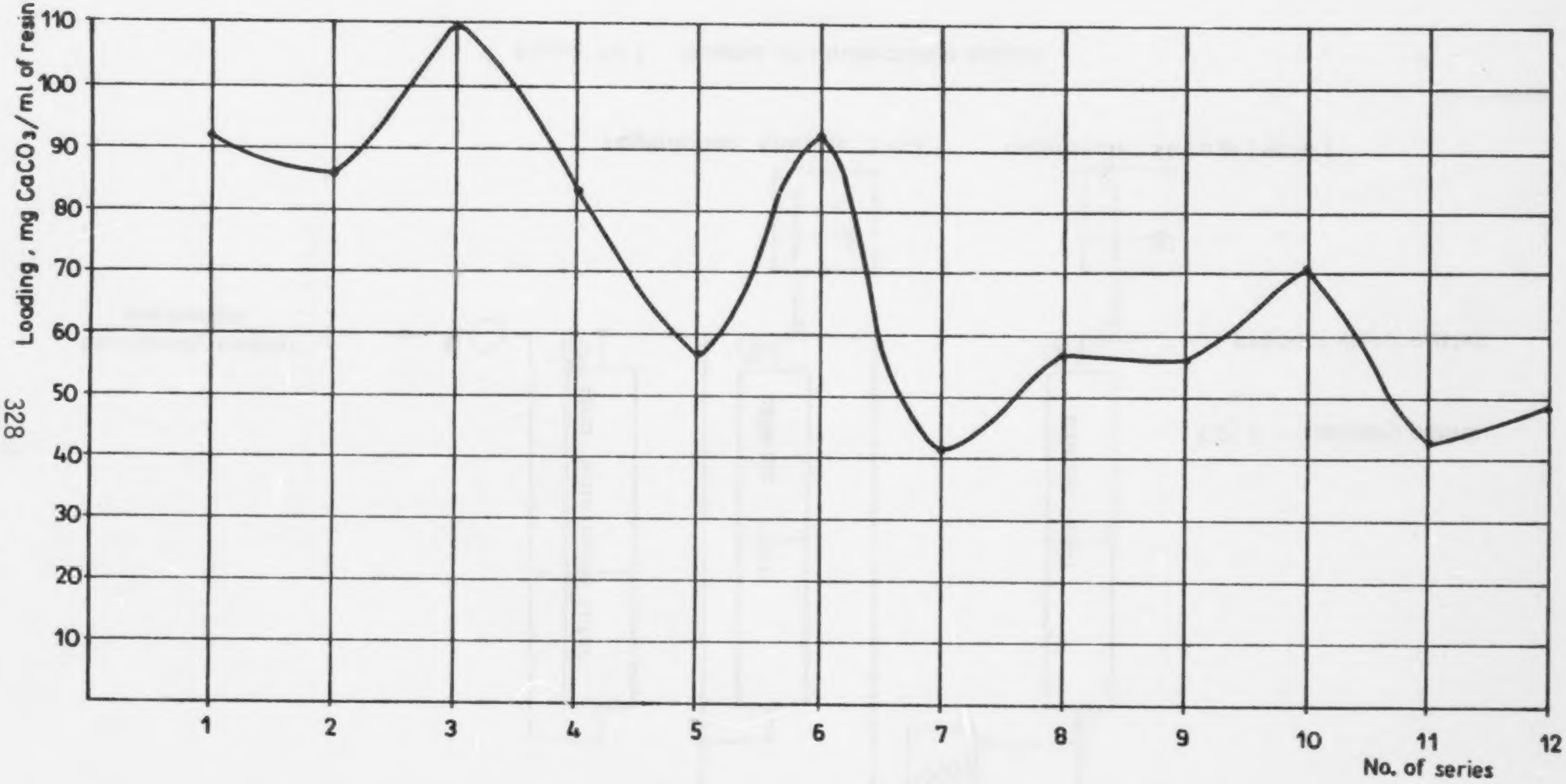


Figure 10-2. Changes of anionic resin (Amberlite IRA - 401) capacity in successive series.

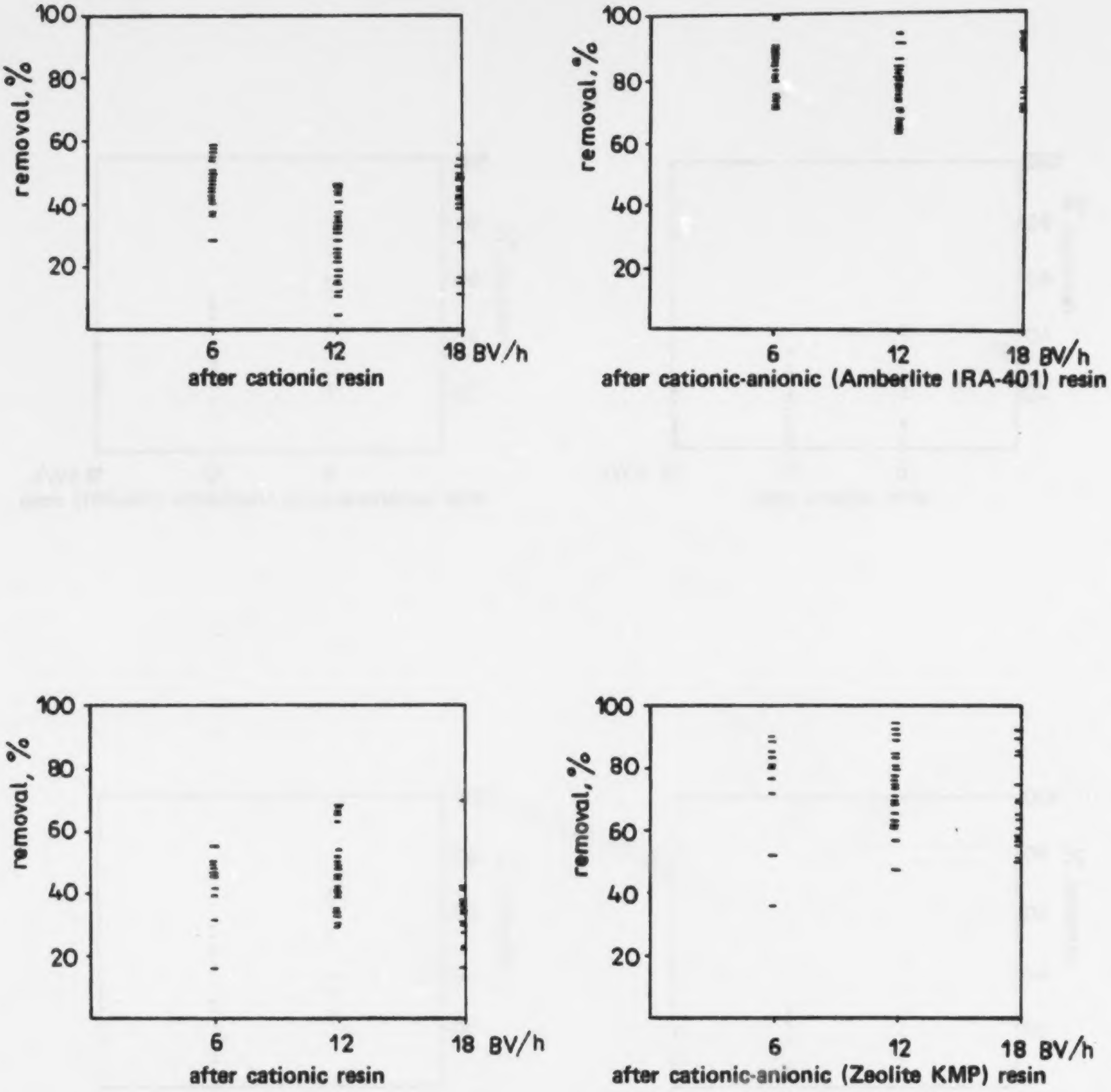
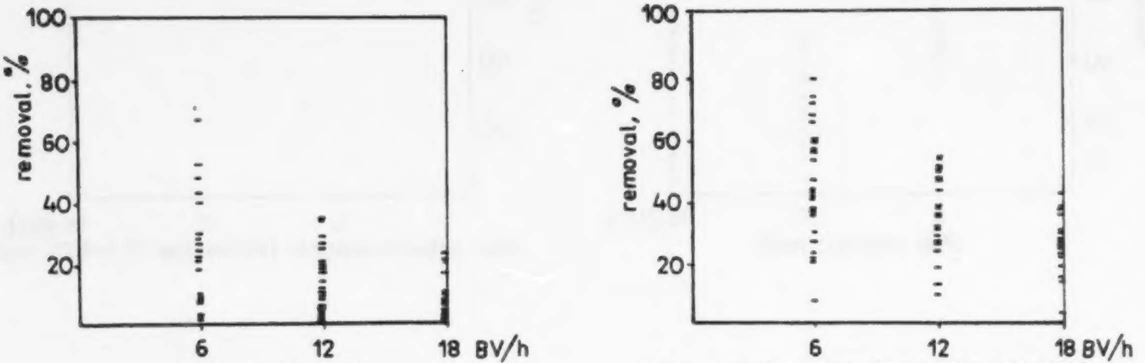
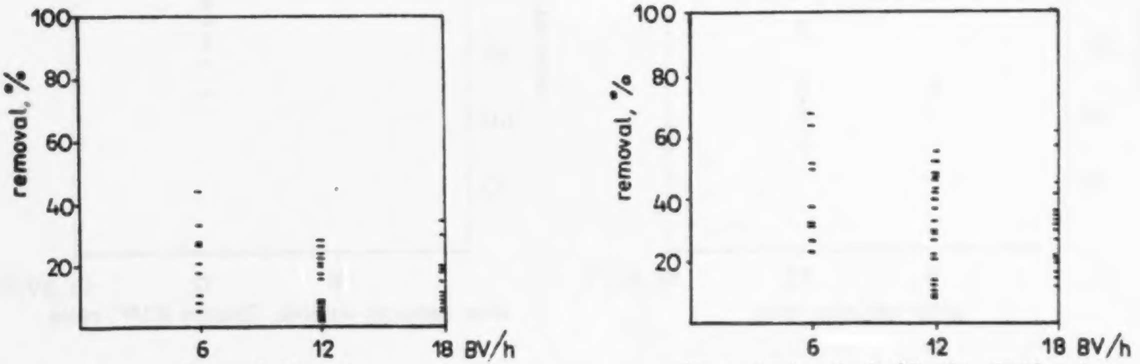


Figure 10-3. Percent color removal versus bed loading (BV/h).



after cationic resin

after cationic-anionic (Amberlite IRA-401) resin



after cationic resin

after cationic-anionic (Zeolite KMP) resin

Figure 10-4. Percent COD removal versus bed loading (BV/h).

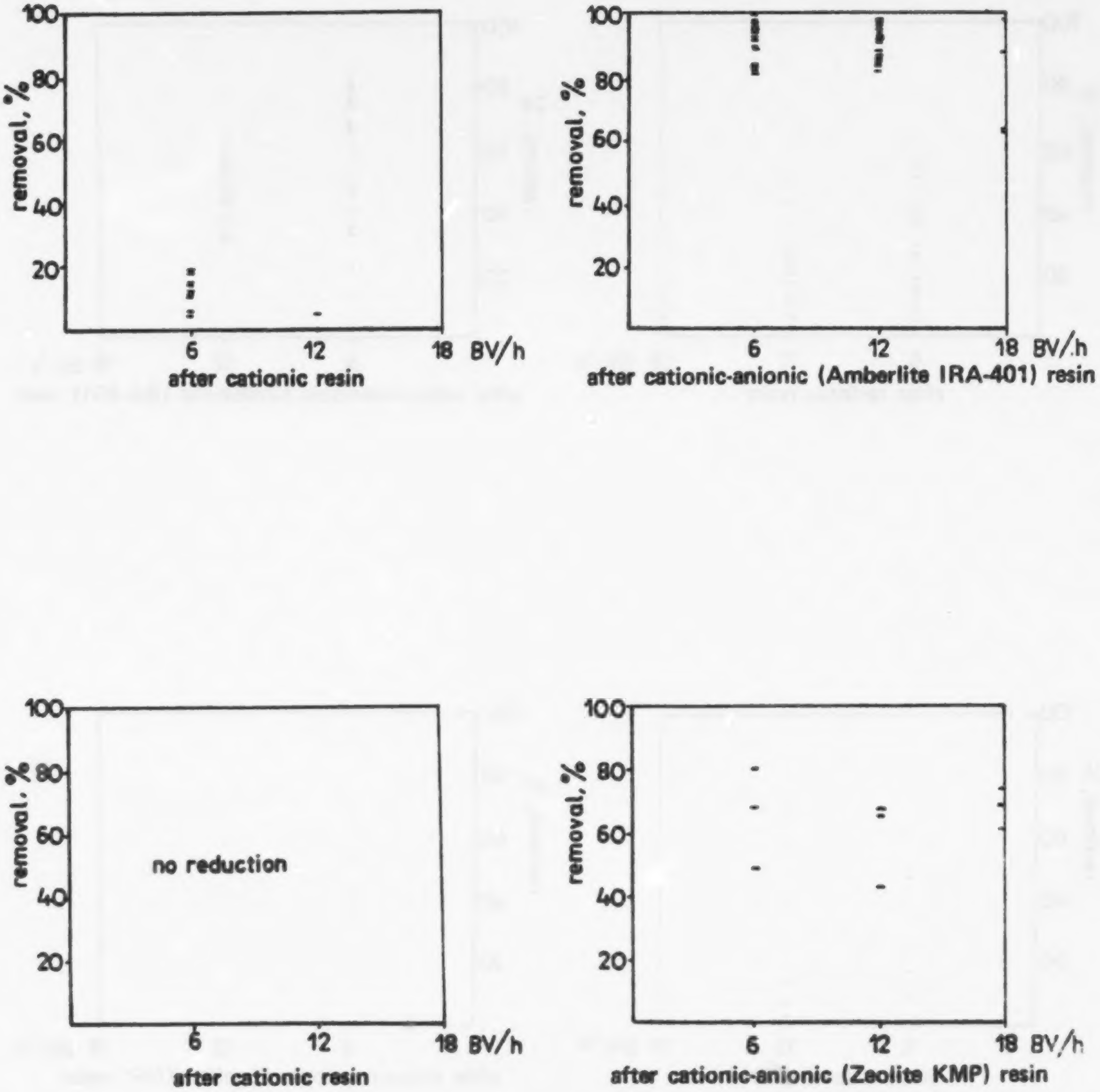
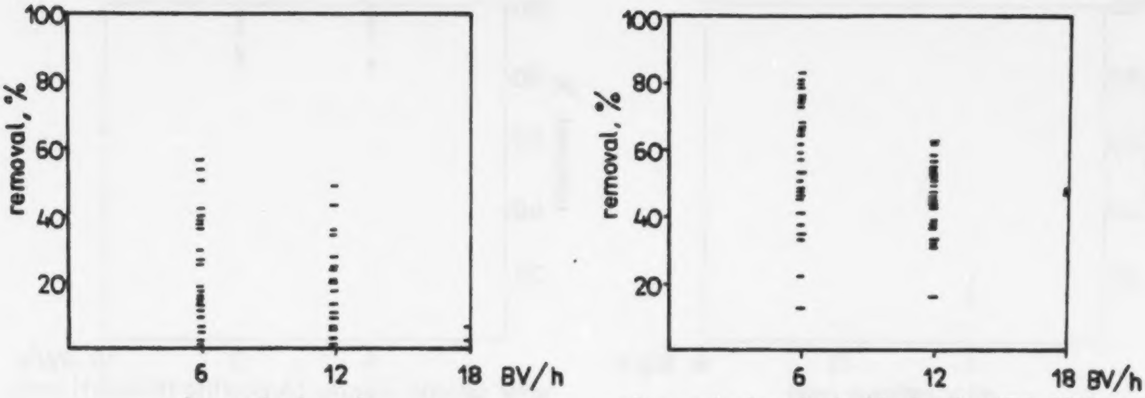
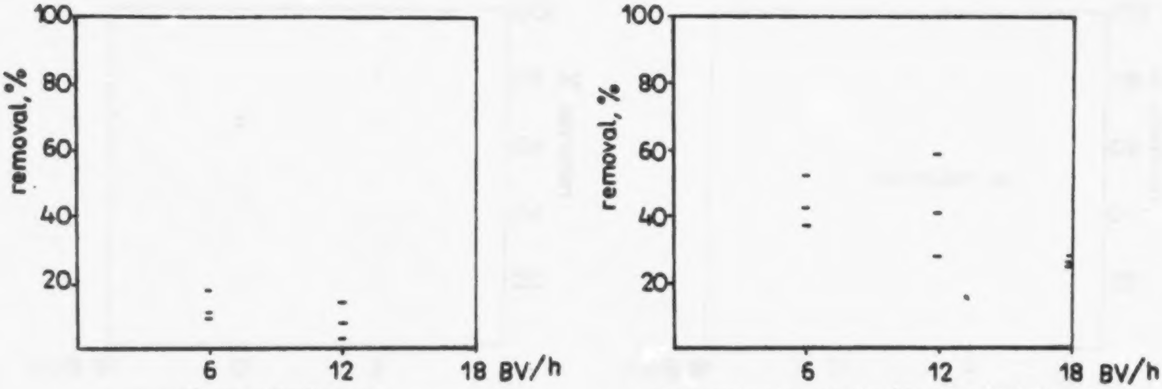


Figure 10-5. Percent anionic detergent removal versus bed loading (BV/h).



after cationic resin

after cationic-anionic (Amberlite IRA-401) resin



after cationic resin

after cationic-anionic (Zeolite KMP) resin

Figure 10-6. Percent nonionic detergent removal versus bed loading (BV/h).

Table 10-1. Seven anionic and five cationic resins used in laboratory screening studies

Anionites		Functional group	Firm
Amberlite IRA-400	Strongly basic	Quaternary ammonium group Type I	SERVA, W. Germany
Amberlite IRA-401	Strongly basic	Quaternary ammonium group Type I	SERVA, W. Germany
Amberlite IRA-410	Strongly basic	Quaternary ammonium group Type I	SERVA, W. Germany
Amberlite IR-45	Weakly basic	Polyamines	SERVA, W. Germany
Zeolite KMP	Strongly basic	Quaternary ammonium group Type I	BDH, England
Zeolite FFIP	Strongly basic	Quaternary ammonium group Type I	BDH, England
Zeolite HXIP	Weakly basic	Polyamines	BDH, England
Cationites			
Amberlite IR-120	Strongly acid	$-SO_3^-$	SERVA, W. Germany
Amberlite IRC-50	Weakly acid	$-COO^-$	SERVA, W. Germany
Zeolite 236	Strongly acid	$-SO_3^-$	BDH, England
Zeolite 325	Weakly acid	$-COO^-$	BDH, England
Zeolite 227	Strongly acid	$-SO_3^-$	BDH, England

Table 10-2. Properties of different resins used in laboratory experiments

Resin	Active groups	Form supplied	Mesh size	Type of regenerant	Exchange capacity meq/ml wet
Amberlite IRA-400 (strongly basic)	Quaternary ammonium type I	Cl^-	14 to 52	NaCl HCl	1.60
Amberlite IRA-401 (strongly basic)	Quaternary ammonium type I	Cl^-	14 to 52	NaCl HCl	1.25
Amberlite IRA 410 (strongly basic)	Quaternary ammonium type I	Cl^-	14 to 52	NaCl HCl	1.60
Amberlite IR-45 (weakly basic)	Polyamine	Cl^-	14 to 52	HCl	2.0
Zeolite KHP (strongly basic)	Quaternary ammonium type I	Cl^-	14 to 52	NaCl HCl	1.0
Zeolite FFIP (strongly basic)	Quaternary ammonium type I	Cl^-	14 to 52	NaCl HCl	1.20
Zeolite HXIP (weakly basic)	Polyamine	Cl^-	14 to 52	HCl	1.70
Amberlite IR-120 (strongly acid)	$-SO_3^-$	Na^+	14 to 52	NaCl	2.10
Amberlite IRC-50 (weakly acid)	$-COO^-$	H^+	14 to 52	HCl H_2SO_4	4.0
Zeolite 325 (strongly acid)	$-SO_3^-$	H^+	14 to 52	HCl H_2SO_4	2.2
Zeolite 236 (weakly acid)	$-COO^-$	H^+	14 to 52	HCl H_2SO_4	3.6
Zeolite 227 (strongly acid)	$-SO_3^-$	Na^+	14 to 52	NaCl	2.1

Table 10-3. Dye-exchange capacity of resins used in laboratory experiments with reference to the best-absorbed dye

Resin	Name of dye	Capacity of dye, mg/ml resin	Bed loading, BV/h
Amberlite IRA-400	Helasol Yellow GOK	6.0	0.12
Amberlite IRA-401	Helasol Yellow GOK	42.50	0.12
Amberlite IRA 410	Helasol Yellow GOK	14.32	0.10
Amberlite IR-45	Salt of Naphthanil Blue BT	2.76	0.05
Zeolite KMP	Helaktyn Yellow D-5GN	17.20	0.10
Zeolite FFIP	Helaktyn Yellow D-5GN	22.59	0.12
Zeolite HXIP	Helaktyn Yellow D-5GN	1.84	0.05
Amberlite IR-120	Salt of Naphthanil Blue BT	0.50	0.12
Amberlite IRC-50	Salt of Naphthanil Blue BT	5.05	0.15
Zeolite 325	Salt of Naphthanil Blue BT	13.0	0.13
Zeolite 236	Salt of Naphthanil Blue BT	2.85	0.11
Zeolite 227	Salt of Naphthanil Blue BT	9.93	0.12

Table 10-4. Decrease in dye capacity after successive regenerations

Number of Regenerations	Amberlite IRA-401 dye Helasol Yellow GOK		Zeolite 325 dye Salt of Naphthanil Blue BT	
	Capacity (mg/l)	Duration of Cycle (h)	Capacity (mg/ml)	Duration of Cycle (h)
0	42.50	60.0	13.00	39.20
1	26.00	36.40	7.77	14.30
2	22.05	21.30	5.50	6.10
3	18.02	15.20	3.59	2.30
4	12.38	10.50	2.79	2.10
5	8.19	6.30	2.22	1.50
6	6.88	4.30	2.11	1.30
7	6.50	4.20	2.08	1.20
8	6.42	4.05	2.07	1.10
9	6.38	3.40	2.06	0.50
10	6.15	3.20	2.04	0.50
11	6.04	3.00	1.98	0.50
12	5.85	2.40	1.92	0.50
13	5.72	2.20	1.88	0.40
14	5.63	2.00	1.86	0.40
15	5.48	1.40	1.84	0.40

Table 10-5. Results of exchange capcity for wastewater investigations

No. of series	Amount of wastewater fed up to exhaustion of anion resin (1)	Alkalinity mg $CaCO_3$/1	Feed alkalinity $CaCO_3$ g	Capacity of anion resin mg $CaCO_3$/ml resin
1	37.8	729.7	27.58	91.9
2	36.0	719.7	25.91	86.4
3	64.8	509.8	33.03	110.1
4	39.9	629.7	25.12	83.8
5	28.8	584.8	16.84	56.1
6	52.4	529.8	27.76	92.5
7	25.9	469.8	12.16	40.6
8	41.2	414.8	17.09	57.0
9	34.6	489.8	16.94	56.5
10	51.7	419.8	21.70	72.4
11	51.3	249.9	12.82	42.7
12	22.8	639.7	11.58	48.6

Table 10-6. Characteristics of wastewater fed to the double ion-exchange system

No. of analysis	1	2	3	4	5	6	7	8	9	10	11	12
pH	8.4	7.9	7.6	8.0	7.75	7.85	8.05	7.9	7.9	7.8	7.6	7.9
Alkalinity, mval/l	14.6	14.4	10.2	12.6	11.7	10.6	9.4	8.3	9.8	8.4	5.0	12.8
Dichromate COD, mg O_2/l	123.6	189.0	154.2	220.0	216.0	114.2	229.2	22.8	54.8	46.1	34.6	163.0
BOD_5, mg O_2/l	38.7	33.6	22.8	31.3	35.8	24.0	39.2	21.3	12.0	17.0	25.0	22.3
Chloride, mg Cl/l	51.1	64.9	64.9	47.5	64.9	121.2	58.1	58.4	51.1	40.3	29.8	49.3
Hardness, total mval/l	1.92	1.80	1.07	2.00	1.78	1.65	2.00	1.79	1.89	2.20	2.00	2.30
Anionic detergents mg/l	0.67	0.75	0.62	0.68	1.41	0.56	0.42	0.60	0.39	0.51	0.23	0.48
Nonionic detergents mg/l	15.0	13.2	15.8	15.3	18.8	14.4	8.0	3.7	6.5	8.5	2.3	17.3

Table 10-7. Regenerator requirements for resins

Type of resin	Ion form	Regenerant solution	$\frac{\text{Regenerant solution (meq)}}{\text{Resin (ml)}}$
Strongly acid cation	H^+	HCl	3 to 5
	Na^+	NaCl	3 to 5
Weakly acid cation	H^+	HCl	1.5 to 2
Strongly basic anion	Cl^-	HCl	4 to 5
Weakly basic anion	Cl^-	HCl	1.5 to 2

Table 10-8. The effectiveness of the single ion-exchange process with anionic resin (Amberlite IRA-401) at a bed loading of 6 BV/h

1 series

	After 4 h			After 8 h			After 12 h			Average sample from a 12-h cycle		
	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %
pH	7.9	7.3		8.0	8.0		7.8	8.3		8.3	8.3	
Alkalinity, meq/l	13.4	6.4		16.0	17.8		17.4	21.2		16.0	16.2	
Permanganate COD, mg O_2/l										24.0	18.0	25.0
BOD_5, mg O_2/l										7.2	4.0	44.4
Dichromate COD, mg O_2/l	78.5	58.6	25.3	78.5	77.9	0.8	100.8	95.5	5.3	87.4	80.3	8.2
Chloride, mg Cl/l	130.9	537.5		64.9	564.0		79.1	135.6		106.5	284.0	
Anionic detergents, mg/l	0.58	0.18	69.0	0.59	0.21	64.4	0.62	0.16	74.2	0.52	0.13	75.0
Nonionic detergents, mg/l	10.9	6.4	41.7	11.9	6.8	43.3	14.2	12.2	14.1	12.3	8.7	29.3
Color, mg Pt/l	200.0	150.0	25.0	150.0	100.0	33.3	200.0	150.0	25.0	200.0	150.0	25.0
Color threshold	5:100	7:100		7:100	10:100		5:100	7:100		5:100	7:100	
Average light absorption, E	0.212	0.138	34.9	0.242	0.181	25.2	0.249	0.201	19.2	0.251	0.185	26.3

Table 10-9. The effectiveness of the single ion-exchange process with anionic resin (Amberlite IRA-401) at a bed loading of 6 BV/h

2 series

	After 4 h			After 8 h			After 12 h			Average sample from a 12-h cycle		
	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %
pH	8.9	8.5		8.9	8.7		8.6	8.3		8.9	8.9	
Alkalinity, meq/l	21.4	11.6		19.8	20.0		12.6	16.4		17.0	16.0	
Permanganate COD, mg O_2/l										33.0	25.0	24.2
BOD_5, mg O_2/l										18.0	10.8	40.0
Dichromate COD, mg O_2/l	131.6	96.8	26.4	94.0	85.5	9.0	90.2	82.7	8.3	105.3	92.1	12.5
Chloride, mg Cl/l	86.2	689.2		107.1	187.6		96.8	117.6		106.5	376.3	
Anionic detergents, mg/l	0.41	0.11	73.2	0.40	0.16	60.0	0.40	0.11	72.5	0.40	0.11	72.5
Nonionic detergents, mg/l	13.7	7.8	43.4	8.4	7.4	12.0	13.9	11.0	14.4	12.0	9.2	23.3
Color, mg Pt/l	250.0	200.0	20.0	200.0	120.0	40.0	200.0	150.0	25.0	220.0	160.0	27.3
Color threshold	3:100	5:100		5:100	8:100		5:100	7:100		4:100	6:100	
Average light absorption, E	0.269	0.128	52.4	0.203	0.175	13.8	0.227	0.156	31.2	0.241	0.179	25.7

Table 10-10. The effectiveness of the single ion-exchange process with anionic resin (Amberlite IRA-401) at a bed loading of 6 BV/h

3 series

	After 4 h			After 8 h			After 12 h			Average sample from a 12-h cycle		
	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %	Influent	After anionic resin	Removal, %
pH	8.6	7.8		8.5	8.5		8.6	8.9		8.6	8.6	
Alkalinity, meq/l	10.2	2.4		13.0	12.0		14.0	17.4		14.2	8.6	
Permanganate COD, mg O_2/l										23.5	11.0	53.2
BOD_5, mg O_2/l										8.5	4.5	47.1
Dichromate COD, mg O_2/l	66.9	58.1	12.3	73.9	54.6	26.2	89.8	63.4	29.4	77.8	55.2	29.0
Chloride, mg Cl/l	100.0	494.0		117.6	294.8		82.6	177.0		88.8	320.0	
Anionic detergents, mg/l	0.48	0.09	81.3	0.55	0.09	83.6	0.59	0.08	86.4	0.54	0.10	81.1
Nonionic detergents, mg/l	9.7	7.3	25.3	13.5	6.9	49.3	10.6	7.4	30.7	11.4	6.7	41.2
Color, mg Pt/l	250.0	100.0	60.0	200.0	80.0	60.0	150.0	60.0	60.0	200.0	80.0	60.0
Color threshold	3:100	10:100		5:100	12:100		7:100	15:100		5:100	12:100	
Average light absorption, E	0.170	0.079	53.5	0.176	0.119	32.4	0.176	0.123	30.1	0.182	0.067	63.2

Table 10-11. Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 6 BV/h

No. of series	Duration of cycle		Amount of treated wastewater
4	24 h		1,627 l
5	20 h		1,356 l
6	24 h		1,627 l
7	32 h		2,169 l
8	20 h		1,356 l
average	24 h	average	1,627 l

Table 10-12. Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 12 BV/h

No. of series	Duration of cycle		Amount of treated wastewater
9	8 h		1,085 l
10	7 h		949 l
11	7 h		949 l
12	5 h		678 l
13	5 h		678 l
average	6 h, 25 min	average	868 l

Table 10-13. Investigations on Zeolite 325 (cation) and Amberlite IRA-401 (anion) at a bed loading of 18 BV/h

No. of series	Duration of cycle		Amount of treated wastewater
14	7 h		1,424 l
15	12 h		2,441 l
16	3 h, 45 min		763 l
average	7 h, 30 min	average	1,543 l

Table 10-14. Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 6 BV/h

No. of series	Duration of cycle		Amount of treated wastewater
17	16 h		1,085 l
18	16 h		1,085 l
19	12 h		814 l
average	14 h, 40 min	average	995 l

Table 10-15. Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 12 BV/h

No. of series	Duration of cycle		Amount of treated wastewater
20	12 h		1,627 l
21	8 h		1,085 l
22	7 h		949 l
average	9 h	average	1,220 l

Table 10-16. Investigations on Zeolite 325 (cation) and Zeolite KMP (anion) at a bed loading of 18 BV/h

No. of eries	Duration of cycle		Amount of treated wastewater
23	9 h		1,831 l
24	4 h, 30 min		915 l
25	4 h, 45 min		763 l
average	5 h, 45 min	average	1,170 l

Table 10-17. Percentage color removal from biologically treated wastewater with dyes of 50 mg/l concentration added, for different anionic exchange resins

Group of dyes	Names of dyes	Amb. IRA-400			Amb. IRA-401			Amb. IRA-410			Amb. IRA-45			Zeolite KMP			Zeolite FFIP			Zeolite HXIP		
		Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h		
		1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0
Sul-furic	Sulphur Black WT	10.9	-	-	26.6	-	-	12.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Sulphur Khaki G	65.1	48.7	-	64.4	64.4	-	61.2	50.0	-	45.7	26.1	22.8	62.5	52.5	72.5	56.5	52.5	65.0	56.2	46.3	61.3
Glacial	Salt of Naphthanil Blue BT	86.1	87.8	54.1	90.4	91.3	59.3	87.8	82.6	59.0	94.5	92.0	91.3	96.5	93.0	80.3	86.0	86.0	68.0	86.0	86.0	85.2
Dis-persed	Synten Rubine P-3B	20.3	-	-	25.0	-	-	22.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Synten Azure	26.9	-	-	32.2	-	-	34.8	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Synten Navy Blue P-BL	21.1	-	-	15.8	-	-	21.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Indanthren Bordeaux RR	20.8	-	-	13.5	-	-	25.0	-	-	35.2	-	-	31.7	-	-	25.6	-	-	23.2	-	-
Reac-tive	Helaktyn Yellow D-5GN	92.6	45.1	13.0	94.6	93.7	95.7	91.6	81.2	33.3	93.2	91.8	69.9	94.7	95.4	94.0	95.4	96.3	93.2	96.2	96.9	96.3
	Helaktyn Yellow DGR	51.7	0.0	-	97.3	93.9	-	91.8	66.0	-	-	-	-	-	-	-	-	-	-	-	-	-
	Drimarene Green X-2BL	29.5	-	-	62.9	-	-	21.9	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Vat	Helanthrene Green BS	17.7	-	-	18.5	-	-	24.6	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Helanthrene Olive BT	7.7	-	-	19.8	-	-	27.4	-	-	19.0	-	-	50.0	-	-	38.9	-	-	51.4	-	-
Indi-gosols	Helasol Grey BT	77.8	63.0	-	83.3	79.6	-	74.1	74.1	-	-	-	-	-	-	-	-	-	-	-	-	-
	Helasol Yellow GGN	88.4	90.8	90.4	91.4	91.4	12.0	90.8	91.8	91.5	99.0	98.2	90.4	94.8	92.2	93.5	92.9	92.9	91.5	96.8	91.6	89.6

Table 10-18. Percentage of color removal from biologically treated wastewater with dyes of 50 mg/l concentration added, for different cationic exchange resins

Group of dyes	Name of dyes	Amb. IR-120			Amb. IRC-50			Zeolite 236			Zeolite 325			Zeolite 227		
		Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h			Bed loading, BV/h		
		1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0	1.5	3.0	6.0
Sulfuric	Sulphur Black WT	-	-	-	4.8	-	-	6.4	-	-	-	-	-	-	-	-
	Sulphur Khaki G	-	-	-	33.6	28.0	-	34.6	44.9	-	52.3	43.9	-	-	-	-
Glacial	Salt of Naphthanil Blue BT	74.2	73.4	0.0	96.8	92.7	91.1	95.2	92.7	91.9	96.0	96.0	95.2	87.9	88.7	87.1
Dispersed	Synten Rubine P-3B	-	-	-	46.3	-	-	61.6	-	-	-	-	-	-	-	-
	Synten Azure	8.2	-	-	14.3	12.2	-	24.5	26.5	-	34.7	26.5	-	44.3	-	-
	Synten Navy Blue P-BL	12.7	-	-	54.8	-	-	51.4	-	-	41.4	-	-	20.6	-	-
	Indanthren Bordeaux RR	9.9	-	-	36.0	-	-	23.0	-	-	47.0	-	-	5.0	-	-
Reactive	Helaktyn Yellow D-5GN	0.0	-	-	0.0	-	-	0.0	-	-	0.0	-	-	9.7	-	-
	Helaktyn Yellow DGR	0.7	-	-	0.0	-	-	0.0	-	-	0.0	-	-	7.4	-	-
	Brimarene Green X-2BL	-	-	-	34.2	-	-	56.1	-	-	40.4	-	-	-	-	-
Vat	Helanthrene Green BS	-	-	-	32.5	-	-	44.4	-	-	25.4	-	-	-	-	-
	Helanthrene Olive BT	-	-	-	28.0	-	-	26.7	-	-	26.7	-	-	-	-	-
Indigosol	Helasol Grey BL	-	-	-	43.8	-	-	53.1	-	-	37.5	-	-	-	-	-
	Helasol Yellow GOK	4.0	-	-	43.0	-	-	4.4	-	-	43.0	-	-	71.3	-	-

Table 10-19. Percentage of color removal from biologically treated wastewater without dyes added

Resin	Bed loading, BV/h		
	1.5	3.0	6.0
Amberlite IRA-400	61.4	55.0	50.8
Amberlite IRA-401	75.2	70.4	68.1
Amberlite IRA-410	68.3	62.0	59.6
Amberlite IR-45	43.1	32.1	11.0
Zeolite KMP	68.3	60.0	55.4
Zeolite FFIP	54.3	50.5	30.4
Zeolite HXIP	70.4	65.8	52.0
Amberlite IR-120	20.3	17.7	10.8
Amberlite IRC-50	40.0	24.0	18.7
Zeolite 325	45.0	41.0	25.1
Zeolite 236	31.0	2.5	0.0
Zeolite 227	18.9	18.2	0.0

Table 10-20. Average percentage of COD removal in the ion-exchange process

Resin	Bed loading, BV/h		
	1.5	3.0	6.0
Amberlite IRA-400	46.4	42.2	23.0
Amberlite IRA-401	50.4	50.9	30.2
Amberlite IRA-410	47.1	47.2	22.6
Amberlite IR-45	30.0	28.0	28.0
Zeolite KMP	50.0	45.0	32.7
Zeolite FFIP	58.4	48.4	35.6
Zeolite HXIP	25.0	12.1	6.0
Amberlite IR-120	15.1	17.5	21.5
Amberlite IRC-50	29.1	28.8	36.5
Zeolite 325	27.4	33.5	51.2
Zeolite 236	45.4	49.9	59.7
Zeolite 227	30.9	20.6	31.4

Table 10-21. Average percentage of anionic detergent removal in the ion-exchange process

Resin	Bed loading, BV/h 1.5	3.0	6.0
Amberlite IRA-400	86.7	80.1	99.0
Amberlite IRA-401	84.6	77.6	99.0
Amberlite IRA-410	82.0	75.6	99.0
Amberlite IR-45	99.0	99.0	99.0
Zeolite KMP	72.9	99.0	99.0
Zeolite FFIP	83.7	99.0	99.0
Zeolite HXIP	100.0	99.0	99.0
Amberlite IR-120	7.8	7.8	6.2
Amberlite IRC-50	57.8	54.1	33.3
Zeolite 325	14.1	16.2	15.2
Zeolite 236	64.5	38.8	27.7
Zeolite 227	17.7	19.9	15.7

Table 10-21. Average percentage of anionic detergent removal in the ion-exchange process

Resin	Bed loading, BV/h 1.5	 3.0	 6.0
Amberlite IRA-400	86.7	80.1	99.0
Amberlite IRA-401	84.6	77.6	99.0
Amberlite IRA-410	82.0	75.6	99.0
Amberlite IR-45	99.0	99.0	99.0
Zeolite KMP	72.9	99.0	99.0
Zeolite FFIP	83.7	99.0	99.0
Zeolite HXIP	100.0	99.0	99.0
Amberlite IR-120	7.8	7.8	6.2
Amberlite IRC-50	57.8	54.1	33.3
Zeolite 325	14.1	16.2	15.2
Zeolite 236	64.5	38.8	27.7
Zeolite 227	17.7	19.9	15.7

Table 10-22. Average percentages of pollutant removal obtained in the ion-exchange process

Specifications	Double system: After cation resin	Double system: After anion resin	Single system after anion resin
Permanganate COD %	15.3	54.1	34.1
Dichromate COD %	21.7	46.2	16.6
Anionic detergents %	0.0	96.3	76.2
Nonionic detergents %	19.1	58.6	31.3
Color on the Pt scale %	36.6	75.0	37.4
Spectrophotometrical color %	50.5	83.6	38.9

Table 10-23. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h

4 series

	After 4-h					After 8-h					After 12-h				
	Influent	After cationic resin	Removal %	After anionic resin	Removal %	Influent	After cationic resin	Removal %	After anionic anion	Removal %	Influent	After cationic resin	Removal %	After anionic resin	Removal %
pH	8.0	2.4		3.4		8.6	2.8		3.3		7.2	2.2		2.2	
Alkalinity, meq/l	14.4					14.3					13.5				
Acidity, meq/l		6.4		6.8			6.2		3.9			5.6		5.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	60.9	47.6	21.8	19.1	68.6	69.3	63.0	9.1	28.0	59.6	75.8	58.1	23.4	40.4	46.7
Chloride, mg Cl/l	72.0	114.2		178.0		79.1	86.2		121.3		82.6	138.8		249.2	
Anionic detergents, mg/l	0.36	0.43	0.0	0.00	100.0	0.34	0.41	0.0	0.00	100.0	0.37	0.33	10.8	0.03	91.9
Nonionic detergents, mg/l	7.8	7.4	5.1	2.9	34.6	10.5	5.2	50.5	2.5	76.2	4.6	4.5	2.2	4.0	13.0
Color, mg Pt/l	80.0	50.0	37.5	15.0	81.3	80.0	50.0	37.5	15.0	81.3	.0	40.0	33.3	15.0	75.0
Color threshold	12:100	20:100		60:100		12:100	20:100		60:100		15:100	25:100		60:100	
Average light absorption, E	0.100	0.050	50.0	0.010	90.0	0.102	0.058	43.1	0.016	84.3	0.100	0.059	41.0	0.018	82.0

Table 10-23 (con.)

	After 16-h					After 20-h					After 24-h				
	Influent	After cationic resin	Removal %	After anionic resin	Removal %	Influent	After cationic resin	Removal %	After anionic resin	Removal %	Influent	After cationic resin	Removal %	After anionic resin	Removal %
pH	7.3	2.2		2.2		7.3	2.2		2.2		8.3	3.4		3.0	
Alkalinity, meq/l	13.1					12.9					11.2				
Acidity, meq/l		6.0		5.8			5.5		5.4			3.4		4.7	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	48.0	50.0	0.0	48.0	0.0	56.0	61.0	0.0	43.0	23.2	51.0	53.4	0.0	22.0	56.9
Chloride, mg Cl/l	79.1	128.4		228.0		72.0	109.8		213.8		59.9	58.1	3.0	284.7	
Anionic detergents, mg/l	0.18	0.32	0.0	0.02	88.9	0.25	0.32	0.0	0.01	96.0	0.25	0.27	0.0	0.04	84.0
Nonionic detergents, mg/l	5.4	4.6	14.8	3.2	40.7	3.3	3.8	0.0	1.3	60.6	3.3	5.8	0.0	2.2	33.3
Color, mg Pt/l	60.0	40.0	33.3	15.0	75.0	80.0	50.0	37.5	15.0	81.3	100.0	60.0	40.00	15.0	85.0
Color threshold	15:100	25:100		60:100		12:100	20:100		60:100		10:100	15:100		60:100	
Average light absorption, E	0.091	0.052	42.9	0.017	81.3	0.052	0.029	44.2	0.000	100.0	0.069	0.049	29.0	0.000	100.0

Table 10-23 (con.)

	Average sample from a 24-h cycle				
	Influent	After cationic resin	Removal %	After anionic resin	Removal %
pH	7.9	2.4		2.5	
Alkalinity, mval/l	14.0				
Acidity, mval/l		5.3		4.2	
Permanganate COD, mg O_2/l	17.0	14.0	17.6	9.5	44.1
BOD_5, mg O_2/l	11.0	1.0	90.9	0.6	94.5
Dichromate COD, mg O_2/l	70.7	58.6	17.1	41.4	41.4
Chloride, mg Cl/l	75.5	91.5		91.5	
Anionic detergents, mg/l	0.25	0.39	0.0	0.00	100.0
Nonionic detergents, mg/l	5.2	4.8	7.7	2.4	53.8
Color, mg Pt/l	100.0	60.0	40.0	15.0	85.0
Color threshold	10.100	15:100		60:100	
Average light absorption, E	0.049	0.024	51.0	0.000	100.0

Table 10-24. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h

5 series

	After 4 h					After 8 h					After 12 h				
	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %
pH	7.6	2.4		2.3		7.7	2.3		2.3		7.8	2.3		2.3	
Alkalinity, meq/l	12.0					12.2					10.8				
acidity, meq/l		11.4		11.2			7.8		8.4			7.4		7.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	84.5	78.0	7.6	47.0	44.4	88.3	80.6	8.7	51.0	42.2	69.1	62.0	10.3	48.0	30.5
Chloride, mg Cl/l	72.0	82.6		256.2		54.6	100.0		64.9		54.6	96.8		227.9	
Anionic detergents, mg/l	0.46	0.77	0.0	0.00	100.0	0.58	0.70	0.0	0.02	96.5	0.64	0.72	0.0	0.00	100.0
Nonionic detergents, mg/l	8.0	5.0	37.5	2.0	75.0	8.8	7.2	18.2	4.1	53.4	4.5	4.4	2.2	3.5	22.2
Color, mg Pt/l	100.0	80.0	20.0	20.0	80.0	120.0	80.0	33.3	30.0	75.0	100.0	80.0	20.0	20.0	80.0
Color threshold	10:100	12:100		50:100		8:10	12:100		35:100		10:100	12:100		50:100	
Average light absorption, E	0.153	0.067	56.2	0.016	89.5	0.176	0.075	57.4	0.027	84.7	0.335	0.084	74.9	0.056	83.3

Table 10-24 (con.)

	After 16 h					After 20 h					Average sample from a 20-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	2.3		2.0		7.3	1.7		2.1		7.6	2.6		2.4	
Alkalinity, meq/l	10.8					11.0					10.8				
Acidity, meq/l		7.4		7.0			6.6		6.4			3.1		3.2	
Permanganate COD, mg O_2/l											19.5	18.5	5.1	9.0	53.8
BOD_5, mg O_2/l											10.0	0.8	92.0	0.8	92.0
Dichromate COD, mg O_2/l	84.5	61.4	27.3	48.0	43.2	63.4	61.4	3.2	39.0	38.5	84.0	59.0	29.8	43.0	48.8
Chloride, mg Cl/l	54.6	100.0		224.4		44.0	110.0		199.6		56.8	78.1		237.8	
Anionic detergents, mg/l	0.70	0.66	5.7	0.04	94.3	0.67	0.64	4.5	0.00	100.0	0.69	0.69	0.0	0.00	100.0
Nonionic detergents, mg/l	6.0	5.6	6.7	3.2	46.7	4.8	6.0		2.0		6.1	5.7	6.6	2.9	52.5
Color, mg Pt/l	100.0	60.0	40.0	20.0	80.0	100.0	60.0	40.0	20.0	80.0	120.0	80.0	33.3	20.0	83.3
Color threshold	10:100	15:100		50:100		10:100	15:100		50:100		8:100	12:100		50:100	
Average light absorption,E	0.178	0.093	47.8	0.031	82.6	0.178	0.099	44.4	0.034	80.9	0.183	0.059	67.8	0.021	88.5

Table 10-25. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h

6 series

	After 4 h					After 8 h					After 12 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	2.0		1.7		7.2	2.1		1.7		7.3	1.8		1.8	
Alkalinity, meq/l	12.6					14.2					17.2				
Acidity, meq/l		7.4		6.8			6.6		7.2			6.2		6.0	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	58.0	44.0	24.1	23.0	60.3	102.0	52.0	49.0	47.0	53.9	54.0	48.0	11.1	42.0	22.2
Chloride, mg Cl/l	79.1	79.1		249.2		68.4	79.1		249.2		72.0	64.9	9.9	235.1	
Anionic detergents, mg/l	0.26	0.25	3.8	0.00	100.0	0.30	0.30	0.0	0.02	93.3	0.37	0.38	0.0	0.015	95.9
Nonionic detergents, mg/l	6.0	3.5	41.7	1.5	75.0	4.95	4.0	19.2	2.7	45.5	6.8	3.1	54.4	2.8	58.8
Color, mg Pt/l	100.0	60.0	40.0	40.0	60.0	120.0	80.0	33.3	40.0	66.7	100.0	60.0	40.0	35.0	65.0
Color threshold	10:100	15:100		25:100		8:100	12:100		25:100		10:100	15:100		30:100	
Average light absorption, E	0.174	0.071	59.2	0.021	87.9	0.195	0.089	54.4	0.033	83.1	0.230	0.095	58.7	0.028	87.8

Table 10-25 (con.)

	After 16 h					After 20 h					After 24 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.0	2.3		2.2		8.0	2.3		2.3		7.9	2.3		2.2	
Alkalinity, meq/l	23.6					22.6					22.4				
Acidity, meq/l		6.8		6.6			6.4		7.2			6.0		6.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	88.0	71.0	19.3	55.0	37.5	102.0	77.0	24.5	41.0	59.8	82.0	88.0	0.0	47.0	42.7
Chloride, mg Cl/l	66.7	79.1		242.1		72.0	75.5		249.2		72.0	68.4	5.0	249.2	
Anionic detergents, mg/l	0.42	0.58	0.0	0.00	100.0	0.55	0.64	0.0	0.02	96.4	0.49	0.55	0.0	0.01	97.9
Nonionic detergents, mg/l	9.7	6.0	38.1	1.8	81.4	7.1	5.2	26.8	2.5	64.8	7.3	6.1	16.4	3.9	46.6
Color, mg Pt/l	120.0	80.0	33.3	25.0	79.2	120.0	80.0	33.3	25.0	79.2	100.0	80.0	20.0	25.0	75.0
Color threshold	8:100	12:100		40:100		8:100	12:100		40:100		10:100	12:100		40:100	
Average light absorption, E	0.232	0.094	59.5	0.021	90.9	0.235	0.060	74.5	0.028	88.1	0.219	0.110	49.8	0.031	85.8

Table 10-25 (con.)

	Average sample from a 24-h cycle				
	Influent	After cationic resin	Removal %	After anionic resin	Removal %
PH	8.1	2.2		2.1	
Alkalinity, mval/l	16.4				
Acidity, mval/l		5.6		5.7	
Permanganate COD, mg O_2/l	24.0	22.5	6.2	8.5	64.6
BOD_5, mg O_2/l	11.5	0.6	94.8	0.8	93.0
Dichromate COD, mg O_2/l	86.0	79.0	8.1	44.0	48.8
Chloride, mg Cl/l	74.6	85.2		248.5	
Anionic detergents, mg/l	0.38	0.50	0.0	0.01	97.4
Nonionic detergents, mg/l	7.1	4.8	32.4	2.7	62.0
Color, mg Pt/l	100.0	60.0	40.0	20.0	80.0
Color threshold	10:100	15:100		50:100	
Average light absorption, E	0.219	0.103	53.0	0.029	86.8

Table 10-26. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h

7 series

	After 4 h					After 8 h					After 12 h				
	Influ-ent	After cationic resin	Remo-val, %	After anionic resin	Remo-val, %	Influ-ent	After cationic resin	Remo-val, %	After anionic resin	Remo-val, %	Influ-ent	After cationic resin	Remo-val, %	After anionic resin	Remo-val, %
pH	8.1	2.9		2.9		7.5	2.4		2.3		7.5	2.4		2.3	
Alkalinity, meq/l	6.8					10.5					14.6				
Acidity, meq/l		5.0		2.3			5.3		4.5			4.5		4.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	69.0	48.0	30.4	14.0	79.7	102.0	48.0	52.9	29.9	71.6	108.0	56.0	48.1	35.0	67.6
Chloride, mg Cl/l	75.5	64.9	14.0	124.8		33.3	64.9		185.4		33.3	64.9		226.0	
Anionic detergents, mg/l	0.26	0.21	19.2	0.00	100.0	0.27	0.22	18.5	0.01	96.3	0.27	0.23	14.8	0.00	100.0
Nonionic detergents, mg/l	5.1	3.1	39.2	2.8	45.1	4.7	3.3	29.8	2.0	57.4	5.8	3.5	39.7	1.0	82.8
Color, mg Pt/l	50.0	30.0	40.0	15.0	70.0	80.0	50.0	37.5	25.0	68.8	80.0	40.0	50.0	20.0	75.0
Color threshold	20:100	35:100		60:100		12:100	20:100		40:100		12:100	25:100		50:100	
Average light absorption, E	0.075	0.043	42.7	0.009	88.0	0.119	0.050	58.0	0.016	86.6	0.157	0.079	49.7	0.020	87.3

Table 10-26 (con.)

	After 16 h					After 20 h					After 24 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	2.3		2.3		7.9	2.3		2.3		8.4	2.5		2.5	
Alkalinity, meq/l	15.8					16.0					17.2				
Acidity, meq/l		4.5		4.4			6.6		6.4			7.0		6.9	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	74.0	44.0	40.5	32.0	56.8	56.0	60.0	0.0	41.0	26.8	200.0	66.0	67.0	52.0	74.0
Chloride, mg Cl/l	33.3	64.9		242.0		68.4	72.0		242.2		64.9	75.5		242.2	
Anionic detergents, mg/l	0.26	0.22	15.4	0.01	96.2	0.32	0.28	12.5	0.02	93.8	0.40	0.34	15.0	0.01	97.5
Nonionic detergents, mg/l	6.4	6.5	0.0	1.3	79.7	4.8	7.3	0.0	2.5	47.9	6.8	6.1	10.3	2.2	67.6
Color, mg Pt/l	80.0	50.0	37.5	25.0	68.8	80.0	50.0	37.5	20.0	75.0	100.0	60.0	40.0	30.0	70.0
Color threshold	12:100	20:100		40:100		12:100	20:100		50:100		10:100	15:100		35:100	
Average light absorption, E	0.178	0.096	46.1	0.028	84.3	0.181	0.092	49.2	0.038	79.0	0.191	0.108	43.5	0.056	70.7

Table 10-26 (con.)

	After 28 h					After 32 h					Average sample from a 32 h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.1	2.1		1.7		7.7	2.0		2.1		7.3	2.2		2.6	
Alkalinity, meq/l	17.4					18.0					10.4				
Acidity, meq/l		8.2		7.4			7.4		7.6			6.6		2.4	
Permanganate COD, mg O_2.1											19.5	15.0	23.1	10.0	48.7
BOD_5, mg O_2/l											10.0	0.6	94.0	0.8	92.0
Dichromate COD, mg O_2/l	72.0	70.0	2.8	46.0	36.1	70.0	64.0	8.6	49.0	30.0	80.0	50.0	37.5	32.0	60.0
Chloride, mg Cl/l	64.9	86.2		270.5		58.1	64.9		291.8		99.4	63.9	35.7	228.2	
Anionic detergents, mg/l	0.53	0.57	0.0	0.10	81.1	0.45	0.45	0.0	0.08	82.2	0.26	0.38	0.0	0.03	88.5
Nonionic detergents, mg/l	9.3	4.0	57.0	2.5	73.1	10.6	5.5	48.1	4.0	62.3	6.7	4.8	28.4	2.3	65.7
Color, mg Pt/l	80.0	50.0	37.5	30.0	62.5	60.0	50.0	16.7	20.0	66.6	60.0	40.0	33.3	20.0	66.0
Color threshold	12:100	20:100		35:100		15:100	20:100		50:100		15:100	25:100		50:100	
Average light absorption, E	0.159	0.099	37.7	0.045	71.1	0.171	0.109	36.3	0.049	71.3	0.127	0.080	37.0	0.037	70.9

Table 10-27. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 6 BV/h

8 series

	After 4 h					After 8 h					After 12 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.4	2.0		1.6		7.1	1.5		1.1		7.2	1.6		1.4	
Alkalinity, meq/l	14.6					18.6					19.8				
Acidity, meq/l		8.8		6.0			8.6		8.8			6.9		7.3	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	85.4	89.2	0.0	36.8	56.9	88.3	92.0	0.0	62.6	29.2	88.3	91.1	0.0	69.9	20.8
Chloride, mg Cl/l	72.0	79.1		236.5		72.0	64.9	9.8	326.6		68.4	72.0		222.4	
Anionic detergents, mg/l	0.42	0.47	0.0	0.02	95.2	0.42	0.37	11.9	0.02	95.2	0.40	0.42	0.0	0.01	97.5
Nonionic detergents, mg/l	13.2	11.6	12.1	2.8	78.8	13.7	8.65	36.9	4.65	66.1	10.6	9.2	13.7	5.6	47.6
Color,	100.0	60.0	40.0	30.0	70.0	100.0	60.0	40.0	40.0	50.0	100.0	60.0	40.0	40.0	60.0
Color threshold	10:100	15:100		35:100		10:100	15:100		25:100		10:100	15:100		25:100	
Average light absorption, E	0.222	0.098	55.8	0.033	85.1	0.231	0.121	47.4	0.036	84.3	0.243	0.128	47.3	0.059	75.7

Table 10-27 (con.)

	After 16 h					After 20 h					Average sample from a 20 h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.3	1.6		1.5		7.5	1.7		1.6		8.4	2.3		2.8	
Alkalinity, meq/l	21.0					22.5					19.2				
Acidity, meq/l		6.4		7.1			7.2		6.2			7.4		7.6	
Permanganate COD, mg O_2/l											22.0	17.0	22.0	9.0	59.1
BOD_5, mg O_2/l											7.2	0.4	94.4	0.4	94.4
Dichromate COD, mg O_2/l	88.3	88.3	0.0	55.2	37.5	92.0	88.3	4.0	84.6	8.0	92.0	77.3	16.0	62.6	32.0
Chloride, mg Cl/l	68.4	79.1		250.7		72.0	121.2		238.8		92.3	92.3	0.0	255.0	
Anionic detergents, mg/l	0.34	0.34	0.0	0.00	100.0	0.37	0.40	0.0	0.06	83.8	0.47	0.49	0.0	0.02	95.7
Nonionic detergents, mg/l	8.8	8.9	0.0	5.6	36.6	9.6	7.1	25.7	4.7	51.3	11.0	8.7	20.5	4.5	59.1
Color, mg Pt/l	100.0	pink		50.0	50.0	100.0	pink		50.0	50.0	100.0	pink		40.0	60.0
Color threshold	10:100	5:100		20:100		10:100	3:100		20:100		10:100	8:100		25:100	
Average light absorption, E	0.243	0.136	44.0	0.059	75.7	0.257	0.161	37.4	0.073	71.6	0.248	0.139	43.9	0.070	71.8

Table 10-28. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

9 series

	After 2 h					After 3 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.8	3.8		3.6		9.0	3.8		3.7		9.0	3.7		3.7	
Alkalinity, meq/l	16.0					16.4					16.8				
Acidity, meq/l		5.0		4.82			5.6		5.8			6.2		5.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	134.4	98.4	26.8	62.5	53.5	146.8	96.9	34.0	67.2	54.2	118.0	99.8	15.4	75.3	36.2
Chloride, mg Cl/l	58.1	72.0		236.4		64.9	100.0		229.2		64.9	100.0		229.2	
Anionic detergents, mg/l	0.83	1.17		0.03	96.4	0.86	0.95		0.03	96.5	0.74	0.98		0.01	98.6
Nonionic detergents, mg/l	14.2	7.3	48.6	5.5	61.3	12.5	11.6	7.2	6.8	45.6	14.2	11.6	18.3	7.2	49.3
Color, mg Pt/l	pink	pink		60.0		pink	pink		60.0		pink	pink		60.0	
Color threshold	1:100	2:100		15:100		1:100	2:100		15:100		1:100	2::100		15:100	
Average light absorption, E	0.341	0.195	42.8	0.017	95.0	0.324	0.242	25.3	0.027	91.7	0.336	0.224	33.3	0.052	84.5

Table 10-28 (con.)

	After 5 h					After 6 h					After 7 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	9.0	4.0		3.9		9.0	4.0		4.0		9.1	3.6		3.6	
Alkalinity, meq/l	16.4					16.8					17.2				
Acidity, meq/l		6.0		7.4			6.0		6.4			6.0		5.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	116.7	115.2	1.3	76.8	34.2	99.8	105.9		69.1	30.8	110.7	96.8	12.6	72.2	34.8
Chloride, mg Cl/l	64.9	72.0		208.2		54.6	180.6		208.2		107.1	64.9	39.4	194.0	
Anionic detergents, mg/l	0.71	1.05		0.02	97.2	0.84	1.00		0.02	97.6	0.61	0.96		0.03	95.1
Nonionic detergents, mg/l	13.9	10.6	23.7	6.3	54.7	14.5	14.2	2.1	8.9	38.6	13.5	9.7	28.1	9.1	32.6
Color, mg Pt/l	pink	pink		60.0		pink	pink		60.0		pink	pink		60.0	
Color threshold	1:100	2:100		15:100		1:100	2:100		15:100		1:100	2:100		15:100	
Average light absorption, E	0.350	0.218	37.7	0.058	83.4	0.349	0.227	35.0	0.090	74.2	0.360	0.235	34.7	0.067	81.4

Table 10-28 (con.)

	After 8 h					Average sample from an 8-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	9.1	3.6		3.6		7.9	2.3		2.4	
Alkalinity, meq/l	17.2					16.4				
Acidity, meq/l		5.8		6.0			5.8		6.0	
Permanganate COD, mg O_2/l						28.0	24.5	12.5	12.5	55.4
BOD_5, mg O_2/l						19.2	0.8	95.8	0.4	97.9
Dichromate COD, mg O_2/l	98.3	98.3	0.0	70.7	28.1	98.3	104.4		86.0	12.5
Chloride, mg Cl/l	64.9	54.1	16.6	166.4		99.4	63.9	35.7	284.0	
Anionic detergents, mg/l	0.75	1.05		0.02	97.3	0.75	1.08		0.01	98.7
Nonionic detergents, mg/l	11.9	12.2		8.2	31.1	12.0	11.0	8.3	7.4	38.3
Color, mg Pt/l	pink	pink		60.0		pink	pink		60.0	
Color threshold	1:100	2:100		15:100		1:100	2:100		15:100	
Average light absorption, E	0.334	0.254	24.0	0.078	76.6	0.356	0.229	35.7	0.066	81.5

Table 10-29. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

10 series

	After 2 h					After 3 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	9.3	3.8		3.7		9.3	3.8		3.7		9.3	3.8		3.7	
Alkalinity, meq/l	20.6					20.4					20.0				
Acidity, meq/l		6.4		5.2			6.2		5.6			6.4		6.2	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	129.2	103.7	19.7	93.8	27.4	144.6	103.1	28.7	72.3	50.0	112.3	90.8	19.1	70.8	37.0
Chloride, mg Cl/l	64.9	64.9		229.2		64.9	64.9		229.2		58.1	51.1	12.0	229.2	
Anionic detergents, mg/l	0.43	0.45	0.0	0.03	93.0	0.48	0.50	0.0	0.03	93.8	0.39	0.43	0.0	0.03	92.3
Nonionic detergents, mg/l	13.5	12.5	7.4	7.3	45.9	15.5	12.2	21.3	6.5	58.1	12.7	11.4	10.2	8.6	32.3
Color, mg Pt/l	pink	pink		60.0		pink	pink		60.0		pink	pink		60.0	
Color threshold	1:100	2:100		15:100		1:100	2:100		15:100		1:100	2:100		15:100	
Average light absorption, E	0.254	0.167	34.3	0.040	84.3	0.221	0.196	11.3	0.053	76.0	0.224	0.198	11.6	0.029	87.0

Table 10-29 (con.)

	After 5 h					After 6 h					After 7 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	9.1	3.9		3.8		9.3	3.8		3.7		9.0	4.0		4.0	
Alkalinity, meq/l	19.8					19.6					19.6				
Acidity, meq/l		6.2		5.8			6.4		6.0			5.2		5.0	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	107.7	100.0	7.1	76.9	28.6	89.7	88.2	1.7	64.6	28.0	92.3	87.7	5.0	75.4	18.3
Chloride, mg Cl/l	64.9	64.9		229.2		64.9	64.9		194.0		64.9	100.0		194.0	
Anionic detergents, mg/l	0.45	0.50	0.0	0.03	93.3	0.40	0.42	0.0	0.06	85.0	0.40	0.42	0.0	0.06	85.0
Nonionic detergents, mg/l	15.5	15.5	0.0	8.9	42.6	18.1	15.5	14.4	8.6	52.5	16.5	18.1	0.0	9.4	43.0
Color, mg Pt/l	pink	pink		60.0		pink	pink		60.0		pink	pink		60.0	
Color threshold	1:100	2:100		15:100		1:100	2:100		15:100		1:100	2:100		15:100	
Average light absorption, E	0.225	0.182	19.1	0.056	75.1	0.226	0.188	16.8	0.072	68.1	0.236	0.200	15.3	0.068	71.2

Table 10-29 (con.)

	Average sample from a 7-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.4	2.5		2.7	
Alkalinity, mval/l	20.0				
Acidity, mval/l		6.2		6.0	
Permanganate COD, mg O_2/l	30.5	24.5	19.7	13.5	55.7
BOD_5, mg O_2/l	17.5	1.0	94.3	0.8	95.4
Dichromate COD, mg O_2/l	113.8	90.2	20.7	69.3	39.1
Chloride, mg Cl/l	88.8	78.1	12.0	244.9	
Anionic detergents, mg/l	0.44	0.58	0.0	0.12	72.7
Nonionic detergents, mg/l	15.5	14.4	7.1	8.4	45.8
Color, mg Pt/l	pink	pink		60.0	
Color threshold	1:100	2:100		15:100	
Average light absorption, E	0.228	0.183	19.7	0.048	79.0

Table 10-30. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

11 series

	After 2 h					After 3 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
ph	8.8	3.2		3.2		8.2	3.0		3.0		8.8	3.2		3.0	
Alkalinity, meq/l	20.8					19.4					20.8				
Acidity, meq/l		8.9		7.8			9.2		9.0			9.2		8.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	90.6	79.7	12.0	46.9	48.2	87.5	82.8	5.4	59.4	32.1	77.1	77.1	0.0	69.7	9.6
Chloride, mg Cl/l	75.5	86.2		267.6		79.1	100.0		250.8		82.6	100.0		324.4	
Anionic detergents, mg/l	0.77	0.79	0.0	0.04	94.8	0.69	0.70	0.0	0.04	94.2	0.62	0.59	4.8	0.08	87.1
Nonionic detergents, mg/l	18.1	13.5	25.4	8.6	52.5	19.6	12.5	36.2	8.7	55.6	15.5	8.9	42.6	7.1	54.2
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	3:100	4:100		25:100		3:100	4:100		25:100		3:100	3:100		25:100	
Average light absorption, E	0.250	0.133	46.8	0.047	81.2	0.218	0.146	33.0	0.048	78.0	0.215	0.140	34.9	0.037	82.8

Table 10-30 (con.)

	After 5 h					After 6 h					After 7 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.8	3.1		3.0		8.8	3.2		3.0		8.7	3.1		3.0	
Alkalinity, meq/l	21.0					21.2					21.4				
Acidity, meq/l		8.4		8.6			9.0		8.2			8.0		8.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	88.0	79.1	10.1	44.0	50.0	91.8	82.6	10.0	56.1	38.9	79.1	75.2	4.9	60.6	23.4
Chloride, mg Cl/l	72.0	86.2		289.2		68.4	93.3		267.6		79.1	86.2		296.0	
Anionic detergents, mg/l	0.64	0.66	0.0	0.06	90.6	0.50	0.53	0.0	0.06	88.0	0.51	0.53	0.0	0.07	86.3
Nonionic detergents, mg/l	14.2	13.7	3.5	8.0	43.7	16.0	16.0	0.0	7.7	51.9	15.0	15.0	0.0	8.0	46.7
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	5:100	3:100		25:100		3:100	4:100		25:100		3:100	3:100		25:100	
Average light absorption, E	0.207	0.140	32.4	0.042	79.7	0.220	0.157	28.6	0.075	65.9	0.217	0.169	22.1	0.078	64.1

Table 10-30 (con.)

	Average sample from a 7 h-cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.6	2.5		2.6	
Alkalinity, mval/l	20.6				
Acidity, mval/l		8.6		8.4	
Permanganate COD, mg O_2/l	25.5	22.5	11.8	14.5	43.1
BOD_5, mg O_2/l	9.0	1.0	88.9	0.2	97.8
Dichromate COD, mg O_2/l	87.5	82.6	5.6	48.2	44.9
Chloride, mg Cl/l	70.4	78.1		284.0	
Anionic detergents, mg/l	0.52	0.59	0.0	0.06	88.5
Nonionic detergents, mg/l	16.4	13.4	18.3	8.1	50.6
Color, mg Pt/l	pink	pink		40.0	
Color threshold	3:100	4:100		25:100	
Average light absorption, E	0.	0.168	20.0	0.060	71.4

Table 10-31. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

12 series

	After 2 h					After 3 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.6	3.1		3.0		8.9	3.2		3.0		7.8	3.2		3.1	
Alkalinity, meq/l	26.8					27.0					27.8				
Acidity, meq/l		8.0		7.6			7.3		7.5			7.2		7.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	128.1	96.1	25.0	62.4	51.3	139.3	113.7	18.4	73.7	47.1	132.9	105.7	20.5	84.8	36.2
Chloride, mg Cl/l	64.9	64.9		229.2		64.9	64.9		265.2		58.1	64.9		229.2	
Anionic detergents, mg/l	0.59	0.64	0.0	0.07	87.7	0.45	0.51	0.0	0.08	82.2	0.50	0.56	0.0	0.01	98.0
Nonionic detergents, mg/l	14.5	9.5	34.5	7.1	51.0	12.5	11.1	11.2	4.7	62.4	11.9	12.5	0.0	7.5	37.0
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	1:100	2:100		25:100		1:100	2:100		25:100		1:100	1:200		25:100	
Average light absorption, E	0.475	0.352	25.9	0.142	70.1	0.499	0.413	17.2	0.127	74.5	0.477	0.455	4.6	0.158	66.9

Table 10-31 (con.)

	After 5 h					Average sample from a 5-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.6	3.1		3.0		8.2	2.6		2.4	
Alkalinity, meq/l	27.8					27.0				
Acidity, meq/l		7.6		7.2			3.8		3.4	
Permanganate COD, mg O_2/l						39.5	34.5	12.7	17.0	57.0
BOD_5, mg O_2/l						17.5	0.6	96.6	0.6	96.6
Dichromate COD, mg O_2/l	115.3	112.1	2.8	88.0	23.7	134.9	119.8	11.2	95.5	29.2
Chloride, mg Cl/l	64.9	64.9		265.2		159.7	198.8		298.2	
Anionic detergents, mg/l	0.58	0.58	0.0	0.02	96.6	0.50	0.63	0.0	0.17	66.0
Nonionic detergents, mg/l	10.2	14.2	0.0	8.6	15.7	12.3	11.7	4.9	7.1	42.3
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0	
Color threshold	1:100	2:100		25:100		1:100	2:100		25:100	
Average light absorption, E	0.506	0.423	16.4	0.171	66.2	0.477	0.364	23.7	0.126	73.6

Table 10-32. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

13 series

	After 2 h					After 3 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.8	2.0		2.1		7.7	2.1		2.0		7.6	2.2		2.1	
Alkalinity, meq/l	16.4					16.4					17.0				
acidity, meq/l		5.6		5.4			5.5		5.2			6.0		5.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	104.5	101.0	3.3	58.2	44.3	142.9	92.5	35.3	89.0	37.7	97.2	104.4	-	84.6	13.0
Chloride, mg Cl/l	58.1	79.1		229.2		61.7	64.9		194.0		61.7	79.1		208.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	100.0	80.0	20.0	30.0	70.0	100.0	60.0	40.0	30.0	70.0	100.0	60.0	40.0	30.0	70.0
Color threshold	10:100	12:100		35:100		10:100	15:100		35:100		10:100	15:100		35:100	
Average light absorption, E	0.205	0.115	43.9	0.041	80.0	0.213	0.118	44.6	0.063	70.4	0.190	0.112	41.0	0.067	64.7

Table 10-32 (con.)

	After 5 h					Average sample from 5-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.7	2.0		2.0		8.3	2.7		2.5	
Alkalinity, meq/l	17.6					16.8				
acidity, meq/l		6.2		5.8			5.5		5.6	
Permanganate COD, mg O_2/l						22.0	20.5	6.8	19.0	13.6
BOD_5, mg O_2/l						17.5	1.0	94.3	0.6	96.6
Dichromate COD, mg O_2/l	101.0	97.2	3.8	72.0	28.7	104.4	89.8	14.0	82.8	20.7
Chloride, mg Cl/l	58.1	64.9		213.6		56.8	56.8		205.9	
Anionic detergents, mg/l						0.32	0.37	0.0	0.01	96.9
Nonionic detergents, mg/l						8.6	6.8	20.9	5.4	37.2
Color, mg Pt/l	80.0	50.0	37.5	30.0	62.5	100.0	60.0	40.0	30.0	70.0
Color threshold	12:100	20:100		35:100		10:100	15:100		35:100	
Average light absorption, E	0.214	0.135	36.9	0.078	63.6	0.212	0.118	44.3	0.070	67.0

Table 10-33. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h

14 series

	After 1 h					After 2 h					After 4 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.8	2.2		2.3		7.8	2.2		2.0		7.7	2.2		2.0	
Alkalinity, meq/l	16.6					16.8					18.0				
Acidity, meq/l		7.3		6.6			7.3		6.8			6.8		6.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	188.8	144.1	23.7	59.6	68.4	139.1	144.1		119.2	14.3	139.1	114.3	17.8	87.7	36.9
Chloride, mg Cl/l	68.4	64.9	5.1	75.5		86.2	64.9	24.7	262.7		72.0	64.9	9.9	241.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		red	pink		40.0	
Color threshold	3:100	4:100		25:100		3:100	4:100		25:100		3:100	4:100		25:100	
Average light absorption, E	0.230	0.153	33.5	0.050	78,3	0.232	0.168	27.6	0.057	75.4	0.225	0.192	14.7	0.060	73.3

Table 10-33 (con.)

	After 5 h					After 6 h					After 7 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.7	2.2		1.9		7.5	2.0		2.2		7.6	1.9		1.8	
Alkalinity, meq/l	18.8					19.0					18.2				
Acidity, meq/l		6.4		6.4			7.0		7.2			6.4		6.2	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	122.7	95.4	22.2	75.6	38.4	109.3	127.8		106.2	2.8	143.0	136.8	4.3	108.0	24.5
Chloride, mg Cl/l	68.4	64.9	5.1	274.0		82.6	79.1	4.2	213.2		82.6	79.1	4.2	255.6	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	red	pink		50.0		red	pink		40.0		pink	pink		40.0	
Color threshold	3:100	4:100		20:100		3:100	4:100		25:100		3:100	4:100		25:100	
Average light absorption, E	0.241	0.215	10.8	0.068	71.8	0.255	0.228	10.6	0.071	72.2	0.265	0.219	17.4	0.062	76.6

Table 10-33 (con.)

	Average sample from a 7-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.2	2.4		2.3	
Alkalinity, mval/l	10.8				
Acidity, mval/l		7.5		5.7	
Permanganate COD, mg O_2/l	32.0	31.5	1.6	17.0	46.9
BOD_5, mg O_2/l	18.0	0.3	98.3	0.4	97.8
Dichromate COD, mg O_2/l	119.9	112.9	5.8	92.7	22.7
Chloride, mg Cl/l	85.2	138.6		261.4	
Anionic detergents, mg/l	0.75	0.84		0.09	88.0
Nonionic detergents, mg/l	20.6	19.1	7.3	11.1	46.1
Color, mg Pt/l	pink	pink		40.0	
Color threshold	3:100	4:100		25:100	
Average light absorption, E	0.246	0.187	24.0	0.057	76.8

Table 10-34. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 18 BV/h

15 series

	After 1 h, 30 min					After 3 h					After 4 h, 30 min				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	2.2		2.1		7.5	2.0		2.2		7.5	2.2		2.1	
Alkalinity, meq/l	17.8					18.2					18.6				
Acidity, meq/l		7.2		7.4			6.8		7.2			5.8		6.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	123.9	108.4	12.5	79.1	36.1	125.5	98.0	21.9	87.7	30.1	129.0	118.7	8.0	96.3	25.3
Chloride, mg Cl/l	82.6	107.1		313.0		82.6	93.3		334.4		82.6	93.3		355.6	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	brown	brown		40.0		brown	brown		40.0		brown	brown		40.0	
Color threshold	5:100	7:100		25:100		5:100	6:100		25:100		5:100	7:100		25:100	
Average light absorption, E	0.410	0.168	59.0	0.037	91.0	0.439	0.199	54.7	0.018	95.9	0.455	0.220	51.6	0.025	94.5

Table 10-34 (con.)

	After 6 h					After 7 h, 30 min					After 9 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.7	2.0		1.8		7.6	2.0		1.9		7.6	1.8		2.1	
Alkalinity, meq/l	18.6					18.4					18.0				
Acidity, meq/l		7.4		7.6			7.4		7.6			6.4		7.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	29.9	122.1	6.0	104.9	19.2	132.4	127.3	3.9	92.8	29.9	120.4	125.5		87.7	27.2
Chloride, mg Cl/l	72.0	86.2		262.7		68.4	100.0		156.0		82.6	100.0		262.7	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	brown	brown		40.0		brown	brown		40.0		brown	brown		40.0	
Color threshold	6:100	8:100		25:100		5:100	7:100		25:100		5:100	8:100		25:100	
Average light absorption, E	0.465	0.230	50.5	0.031	93.3	0.459	0.247	46.2	0.035	92.4	0.458	0.240	47.6	0.028	93.9

Table 10-34 (con.)

	After 10 h, 30 min					After 12 h					Average sample from a 12-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	2.5		1.8		7.7	2.0		1.8		7.7	2.5		2.3	
Alkalinity, meq/l	17.8					17.8					18.0				
Acidity, meq/l		6.4		6.4			7.0		6.6			7.4		7.7	
Permanganate COD, mg O_2/l											34.0	30.5	10.3	21.0	38.2
BOD_5, mg O_2/l											23.3	0.3	98.7	0.2	99.1
Dichromate COD, mg O_2/l	122.1	120.4	1.4	70.5	42.3	139.3	139.3	0.0	101.5	27.1	137.6	127.3	7.5	98.0	28.8
Chloride, mg Cl/l	79.1	100.0		313.0		75.5	100.0		306.0		85.2	95.2		258.3	
Anionic detergents, mg/l											0.72	0.75		0.27	62.5
Nonionic detergents, mg/l											20.6	19.9	3.4	10.9	47.1
Color, mg Pt/l	brown	brown		40.0		brown	brown		40.0		brown	brown		40.0	
Color threshold	5:100	8:100		25:100		5:100	7:100		25:100		5:100	7:100		25:100	
Average light absorption, E	0.445	0.229	48.5	0.030	93.3	0.421	0.217	48.5	0.030	92.9	0.434	0.207	52.3	0.026	94.0

Table 10-35. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 18 BV/h

16 series

	After 45 min					After 1 h, 30 min					After 2 h, 15 min				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.3	1.7		1.5		7.2	1.5		1.6		7.2	1.4		1.2	
Alkalinity, meq/l	18.2					17.8					17.6				
Acidity, meq/l		11.4		10.0			11.6		10.8			11.4		11.1	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	127.3	118.3	7.1	94.6	25.7	135.9	120.4	11.4	104.9	22.8	138.6	131.4	5.2	96.3	30.5
Chloride, mg Cl/l	64.9	100.0		383.9		64.9	121.2		255.6		82.6	171.2		205.9	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		red	red		40.0	
Color threshold	8:100	10:100		25:100		8:100	10:100		25:100		4:100	5:100		25:100	
Average light absorption, E	0.327	0.180	45.0	0.021	93.6	0.362	0.221	39.0	0.026	92.8	0.389	0.233	40.1	0.037	90.5

Table 10-35 (con.)

	After 3 h					After 3 h, 45 min					Average sample from a 3-h, 45-min cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.3	1.6		1.3		7.2	1.3		1.3		8.4	2.0		2.0	
Alkalinity, meq/l	17.6					17.4			18.8		18.8				
Acidity, meq/l		11.6		11.0			12.3		11.6			10.1		10.0	
Permanganate COD, mg O_2/l											32.5	31.0	4.6	22.0	32.3
BOD_5, mg O_2/l											13.0	0.7	94.6	0.5	96.2
Dichromate COD, mg O_2/l	140.4	127.8	9.0	109.8	21.8	122.4	118.8	2.9	104.4	14.7	134.2	123.9	7.7	94.6	29.5
Chloride, mg Cl/l	82.6	114.2		403.2		64.9	75.5		313.0		74.6	92.3		418.9	
Anionic detergents, mg/l											0.52	0.67		0.01	98.1
Nonionic detergents, mg/l											20.8	20.8	0.0	11.1	46.6
Color, mg Pt/l	red	red		40.0		red	red		40.0		red	red		40.0	
Color threshold	4:100	7:100		25:100		5:100	6:100		25:100		6:100	7:100		25:100	
Average light absorption, E	0.429	0.247	42.4	0.038	91.1	0.448	0.260	42.0	0.042	90.6	0.406	0.229	43.6	0.032	92.1

Table 10-36. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h

17 series

	After 4 h					After 8 h					After 12 h				
	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %
pH	7.7	2.1		2.0		7.6	1.8		1.8		8.2	2.0		2.0	
Alkalinity, meq/l	13.2					14.3					15.8				
acidity, meq/l		7.7		7.0			7.2		6.8			8.2		6.9	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	88.5	63.8	27.9	128.5		86.8	71.1	18.1	53.8	38.0	92.2	87.6	5.0	61.4	33.4
Chloride, mg Cl/l	82.6	82.6	0.0	193.9		193.9	75.5	61.1	291.6		99.7	100.0		291.6	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		30.0		pink	pink		30.0		pink	pink		30.0	
Color threshold	5:100	7:100		35:100		5:100	7:100		35:100		5:100	7:100		35:100	
Average light absorption, E	0.595	0.302	49.2	0.065	89.1	0.540	0.290	46.3	0.074	86.3	0.493	0.264	46.5	0.048	90.3

Table 10-36 (con.)

	After 16 h					Average sample from a 16-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.4	2.2		2.2		8.3	2.3		2.3	
Alkalinity, meq/l	17.4					15.0				
Acidity, meq/l		8.2		8.9			8.0		7.0	
Permanganate COD, mg O_2/l						30.0	23.5	21.7	15.0	50.0
BOD_5, mg O_2/l						11.5	1.2	89.6	1.0	91.3
Dichromate COD, mg O_2/l	101.4	90.6	10.7	69.1	31.9	116.8	82.9	29.0	66.0	43.5
Chloride, mg Cl/l	100.0	107.1		291.6		95.9	248.5		284.0	
Anionic detergents, mg/l						0.55	0.57		0.11	80.0
Nonionic detergents, mg/l						6.75	6.10	9.6	4.15	38.5
Color, mg Pt/l	red	pink		30.0		pink	pink		30.0	
Color threshold	1:100	3:100		35:100		3:100	5:100		37:100	
Average light absorption, E	0.440	0.220	50.0	0.072	83.6	0.511	0.237	53.6	0.048	90.6

Table 10-37. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h

18 series

	After 4 h					After 8 h					After 12 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.5	2.2		2.2		8.5	2.0		1.8		8.3	2.0		1.8	
Alkalinity, meq/l	21.4					21.6					21.6				
Acidity, meq/l		8.5		5.0			8.6		7.4			8.7		7.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD mg O_2/l	110.9	61.6	44.5	35.2	68.3	73.9	58.1	21.4	26.4	64.3	93.3	123.2	-	96.8	-
Chloride, mg Cl/l	72.0	193.9	-	208.2		82.6	100.0		313.0		75.5	79.1		291.6	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		30.0		pink	pink		30.0		pink	pink		30.0	
Color threshold	1:100	2:100		35:100		1:100	2:100		35:100		1:100	2:100		35:100	
Average light absorption, E	0.274	0.124	54.7	0.052	81.0	0.213	0.129	39.4	0.042	80.3	0.216	0.150	30.6	0.139	35.6

Table 10-37 (con.)

	After 16 h					Average sample from a 16-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.4	2.2		1.9		8.3	2.4		2.4	
Alkalinity, meq/l	21.6					21.6				
Acidity, meq/l		4.8		6.4			7.6		6.8	
Permanganate COD, mg O_2/l						28.5	22.0	22.8	17.0	40.4
BOD_5, mg O_2/l						10.0	1.0	90.0	0.6	94.0
Dichromate COD, mg O_2/l	84.5	91.5		61.6	27.1	84.5	77.4	8.4	56.3	33.4
Chloride, mg Cl/l	82.6	82.6	0.0	355.6		92.3	92.3	0.0	290.1	
Anionic detergents, mg/l						0.52	0.53		0.27	48.1
Nonionic detergents mg/l						17.0	13.9	18.2	9.7	42.9
Color, mg Pt/l	pink	pink		light pink		pink	pink		pink	
Color threshold	0.5:100	1:100		7:100		1:100	2:100		5:100	
Average sample absorption, E	0.203	0.167	17.7	0.097	52.5	0.215	0.130	39.5	0.050	76.7

Table 10-38. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 6 BV/h

19 series

	After 4 h					After 8 h					After 12 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.0	1.5		1.6		8.0	1.8		1.2		7.7	1.7		1.6	
Alkalinity, meq/l	17.4					17.8					17.0				
Acidity, meq/l		14.5		9.7			14.8		12.6			13.8		12.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	140.6	102.6	27.0	68.8	51.1	152.1	101.6	33.2	76.0	50.0	165.0	152.8	7.4	126.8	23.1
Chloride, mg Cl/l	100.0	262.7	-	383.9	-	100.0	208.2		560.2		89.7	193.9		524.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	light brown	light brown		50.0		brown	light brown		120.0		brown	light brown		light brown	
Color threshold	2:100	3:100		20:100		2:100	3:100		8:100		2:100	3:100		5:100	
Average light absorption, E	0.442	0.230	48.0	0.070	84.2	0.624	0.323	48.2	0.144	76.9	0.647	0.380	41.3	0.183	71.7

Table 10-38 (con.)

	Average sample from a 12-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	8.1	2.3		2.3	
Alkalinity, mval/l	17.0				
Acidity, mval/l		14.6		10.1	
Permanganate COD, mg O_2/l	38.0	37.5	1.3	26.0	31.6
BOD_5, mg O_2/l	26.7	1.0	96.3	0.8	97.0
Dichromate COD, mg O_2/l	143.6	121.1	15.7	76.0	47.1
Chloride, mg Cl/l	85.2	140.2		461.5	
Anionic detergents, mg/l	0.79	0.83		0.26	67.1
Nonionic detergents, mg/l	13.5	11.9	11.9	6.5	51.9
Color, mg Pt/l	brown	brown		light brown	
Color threshold	2:100	3:100		10:100	
Average light absorption, E	0.576	0.268	53.5	0.120	79.2

Table 10-39. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h

20 series

	After 2 h					After 4 h					After 6 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.8	2.2		2.2		7.8	2.2		2.1		7.5	2.1		1.9	
Alkalinity, meq/l	9.1					10.8					9.6				
Acidity, meq/l		6.3		5.6			6.2		5.4			6.0		5.9	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	107.8	82.6	23.4	52.0	51.8	89.3	82.2	4.6	77.0	13.8	83.7	82.3	1.7	61.1	27.0
Chloride, mg Cl/l	75.5	82.6		193.9		82.6	117.6		193.9		64.9	156.0		213.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	80.0		30.0		pink	80.0		30.0		pink	80.0		30.0	
Color threshold	5:100	12:100		35:100		4:100	12:100		35:100		5:100	12:100		35:100	
Average light absorption, E	0.478	0.238	50.2	0.090	81.2	0.429	0.204	52.4	0.085	80.2	0.424	0.196	53.8	0.096	77.4

Table 10-39 (con.)

	After 8 h					After 10 h					After 12 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	2.1		2.0		7.6	2.1		2.0		7.5	2.2		2.2	
Alkalinity, meq/l	9.8					9.8					8.5				
Acidity, meq/l		6.6		6.2			6.0		5.9			7.2		6.7	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	100.0	92.4	8.3	78.4	22.2	93.8	91.0	3.0	84.0	10.4	93.4	87.0	6.9	85.8	8.1
Chloride, mg Cl/l	82.6	86.3		248.5		72.0	86.3		281.2		82.6	100.0		283.0	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	100.0	100.0	0.0	50.0	50.0	100.0	100.0	0.0	60.0	40.0	100.0	100.0	0.0	60.0	40.0
Color threshold	10:100	12:100		20:100		10:100	10:100		15:100		10:100	10:100		15:100	
Average light absorption, E	0.416	0.217	47.8	0.110	73.6	0.403	0.201	50.1	0.090	77.7	0.405	0.220	45.7	0.117	71.1

Table 10-39 (con.)

	Average sample from a 12 h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.8	2.4		2.3	
Alkalinity, mval/l	10.8				
Acidity, mval/l		6.6		6.1	
Permaganate COD, mg O_2/l	25.0	25.0	0.0	22.5	10.0
BOD_5, mg O_2/l	15.0	0.8	94.7	0.9	94.0
Dichromate COD, mg O_2/l	90.3	81.0	10.3	73.0	19.2
Chloride, mg Cl/l	78.1	106.5		230.7	
Anionic Detergents, mg/l	0.81	0.83		0.82	65.4
Nonionic detergents, mg/l	9.8	0.4	4.1	5.8	40.8
Color, mg Pt/l	120.0	100.0	16.7	60.0	50.0
Color threshold	8:100	10:100		15:100	
Average light absorption, E	0.413	0.210	49.2	0.093	77.5

Table 10-40. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h

21 series

	After 1 h					After 2 h					After 3 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	2.2		2.1		7.5	2.2		2.1		7.6	2.2		2.0	
Alkalinity, meq/l	13.3					14.2					8.8				
idity, meq/l		8.4		6.7			8.2		8.6			9.6		8.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	107.5	76.8	28.6	48.6	54.8	110.1	83.2	24.4	64.0	41.9	95.5	80.3	15.9	67.8	29.0
Chloride, mg Cl/l	82.6	82.6	0.0	225.6		75.5	79.1		313.0		64.9	64.9	0.0	306.0	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	140.0	90.0	35.7	50.0	64.3	120.0	100.0	16.7	50.0	58.3	120.0	50.0	58.3	50.0	58.3
Color threshold	5:100	10:100		20:100		8:100	10:100		20:100		8:100	20:100		20:100	
Average light absorption, E	0.449	0.224	50.1	0.112	75.1	0.470	0.225	45.7	0.140	70.2	0.282	0.173	38.7	0.150	46.8

Table 10-40 (con.)

	After 4 h					After 5 h					After 6 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	1.7		1.6		7.6	1.7		1.6		7.7	1.7		1.6	
Alkalinity, meq/l	15.2					17.4					18.2				
Acidity, meq/l		9.2		9.6			9.6		9.6			9.4		9.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	121.8	116.3	4.5	85.8	29.6	143.9	135.6	5.8	100.9	29.9	133.2	133.6	-	121.8	8.6
Chloride, mg Cl/l	64.9	86.3		355.6		68.4	93.3		341.2		64.9	93.3		306.0	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	140.0	140.0	0.0	60.0	57.1	140.0	120.0	14.3	60.0	57.1	140.0	120.0	14.3	60.0	57.1
Color threshold	5:100	5:100		15:100		5:100	7:100		15:100		5:100	7:100		15:100	
Average light absorption, E	0.526	0.310	41.1	0.182	65.4	0.583	0.383	34.3	0.223	61.7	0.596	0.402	32.6	0.220	63.1

Table 10-40 (con.)

	After 7 h					After 8 h					Average sample from an 8-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	1.6		1.6		7.6	1.6		1.6		8.0	2.6		2.5	
Alkalinity, meq/l	18.2					19.0					16.0				
Acidity, meq/l		9.6		9.2			10.0		9.6			9.2		9.0	
Permanganate COD, mg O_2/l											30.5	28.0	8.2	24.5	19.7
BOD_5, mg O_2/l											15.0	0.4	97.3	0.6	96.0
Dichromate COD, mg O_2/l	150.4	148.9	1.0	118.8	21.0	161.7	167.5		141.8	12.3	125.9	116.2	7.7	94.1	25.3
Chloride, mg Cl/l	72.0	100.0		376.8		72.0	100.0		376.8		74.6	88.8		355.0	
Anionic detergents, mg/l											0.67	0.69		0.39	41.8
Nonionic detergents, mg/l											11.4	9.7	14.9	8.2	28.1
Color, mg Pt/l	140.0	120.0	14.3	60.0	57.1	140.0	120.0	14.3	60.0	57.1	140.0	140.0		60.0	57.1
Color threshold	5:100	7:100		15:100		5:100	7:100		15:100		5:100	5:100		15:100	
Average light absorption, E	0.620	0.438	29.4	0.237	61.8	0.642	0.455	29.1	0.250	61.1	0.519	0.254	51.1	0.110	78.8

Table 10-41. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 12 BV/h

22 series

	After 1 h					After 2 h					After 3 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	1.7		1.6		7.7	1.7		1.7		7.5	1.8		1.7	
Alkalinity, meq/l	21.8					23.8					22.4				
Acidity, meq/l		11.4		8.6			12.6		11.6			15.8		13.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	179.0	131.7	26.4	93.1	48.0	199.0	157.5	20.9	104.3	47.6	183.3	147.5	19.5	98.8	46.1
Chloride, mg Cl/l	72.0	121.3		348.4		72.0	171.2		453.2		68.4	262.7		457.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	3:100	5:100		25:100		3:100	4:100		25:100		3:100	4:100		25:100	
Average light absorption, E	0.585	0.215	63.2	0.027	95.4	0.584	0.192	67.1	0.039	93.3	0.547	0.172	68.5	0.090	83.5

Table 10-41 (con.)

	After 4 h					After 5 h					After 6 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.4	1.8		1.9		7.5	1.5		1.7		7.5	1.9		1.5	
Alkalinity, meq/l	20.8					20.8					20.8				
Acidity, meq/l		17.2		13.4			17.0		15.2			16.0		14.6	
Permanganate COD, mg O_2/l															
Dichromate COD, mg O_2/l	199.0	164.7	17.2	119.1	40.2	192.0	195.6		127.9	33.4	212.0	204.8	3.4	120.6	43.1
Chloride, mg Cl/l	64.9	135.6		457.2		68.4	107.1		524.2		72.0	93.3		560.2	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		red	pink		40.0	
Color threshold	2:100	4:100		25:100		2:100	4:100		25:100		2:100	4:100		25:100	
Average light absorption, E	0.533	0.180	66.2	0.046	91.4	0.493	0.171	65.3	0.055	88.8	0.455	0.157	65.5	0.067	95.3

Table 10-41 (con.)

	After 7 h					Average sample from a 7-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	1.8		1.9		8.2	2.7		2.4	
Alkalinity, meq/l	20.8					20.8				
Acidity, meq/l		16.6		13.8			12.6		12.2	
Permanganate COD, mg O_2/l						40.5	40.5	0.0	28.0	30.9
BOD_5, mg O_2/l						23.0	0.5	97.8	0.4	98.3
Dichromate COD, mg O_2/l	216.2	202.4	6.4	136.7	36.8	192.0	189.0	1.6	113.6	40.8
Chloride, mg Cl/l	82.6	193.9		560.2		71.0	88.8		532.5	
Anionic detergents, mg/l						0.86	0.88		0.28	67.4
Nonionic detergents, mg/l						19.9	18.1	9.0	8.2	58.8
Color, mg Pt/l	red	pink		40.0		red	pink		40.0	
Color threshold	2:100	4:100		25:100		2:100	4:100		25:100	
Average light absorption, E	0.392	0.232	40.8	0.096	75.5	0.529	0.524	0.9	0.057	89.2

Table 10-42. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h

23 series

	After 1 h, 30 min					After 3 h					After 4 h, 30 min				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.7	2.0		2.0		7.6	2.1		2.2		7.1	2.1		1.9	
Alkalinity, meq/l	9.2					9.0					8.6				
Acidity, meq/l		5.4		5.6			5.0		5.2			4.6		4.8	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	86.4	79.2	8.3	55.8	35.4	86.7	78.0	10.0	49.9	42.4	69.4	56.6	18.4	45.5	34.4
Chloride, mg Cl/l	54.6	79.1		192.6		47.5	86.2		178.3		61.7	114.2		185.4	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		30.0		pink	pink		30.0		pink	pink		30.0	
Color threshold	8:100	8:100		35:100		8:100	8:100		35:100		9:100	12:100		35:100	
Average light absorption, E	0.160	0.094	41.3	0.050	68.8	0.136	0.089	34.6	0.058	57.4	0.141	0.100	27.1	0.051	63.8

Table 10-42 (con.)

	After 6 h					After 7 h, 30 min					After 9 h				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.1	1.8		1.8		7.2	2.1		1.7		7.3	2.1		1.9	
Alkalinity, meq/l	7.4					7.8					6.7				
Acidity, meq/l		4.2		4.6			4.8		5.0			4.2		4.4	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	54.2	56.6		43.4	19.9	65.0	65.0	0.0	54.2	16.6	91.0	73.7	19.0	63.7	30.0
Chloride, mg Cl/l	47.5	72.0		171.2		54.6	86.2		192.6		47.5	79.1		164.1	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		35.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	10:100	12:100		30:100		8:100	8:100		25:100		15:100	20:100		25:100	
Average light absorption, E	0.130	0.086	33.8	0.040	69.2	0.140	0.098	30.0	0.049	65.0	0.132	0.092	30.3	0.055	58.3

Table 10-42 (con.)

	Average sample from a 9-h cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.7	2.7		2.6	
Alkalinity, mval/l	8.0				
Acidity, mval/l		4.8		4.9	
Permanganate COD, mg O_2/l	22.5	16.5	26.7	12.5	44.4
BOD_5, mg O_2/l	21.0	0.3	98.6	0.3	98.6
Dichromate COD, mg O_2/l	96.2	73.7	23.4	58.5	39.2
Chloride, mg Cl/l	60.4	88.8		230.7	
Anionic detergents, mg/l	0.42	0.47		0.11	73.8
Nonionic detergents, mg/l	14.5	14.4	0.7	10.4	28.3
Color, mg Pt/l	pink	pink		40.0	
Color threshold	5:100	6:100		25:100	
Average light absorption, E	0.137	0.103	24.8	0.056	59.1

Table 10-43. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h

24 series

	After 45 min					After 1 h, 30 min					After 2 h, 15 min				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.4	1.9		1.9		7.7	2.0		2.0		7.6	2.0		1.8	
Alkalinity, meq/l	16.8					17.0					17.4				
acidity, meq/l		9.6		7.0			8.6		8.6			8.6		9.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	166.9	134.4	19.5	62.9	62.3	182.1	156.1	14.3	119.2	34.5	200.0	162.6	18.6	136.6	31.7
Chloride, mg Cl/l	72.0	79.1		270.3		82.6	100.0		313.0		79.1	93.3		313.0	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		50.0	
Color threshold	1:100	2:100		25:100		1:100	2:100		25:100		1:100	1:100		20:100	
Average light absorption, E	0.421	0.268	36.3	0.030	92.9	0.404	0.313	22.5	0.100	75.2	0.492	0.309	37.2	0.151	69.3

Table 10-43 (con.)

	After 3 h					After 3 h, 45 min					After 4 h, 30 min				
	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %	Influ-ent	After cationic resin	Remov-al, %	After anionic resin	Remov-al, %
pH	7.6	1.9		2.0		7.5	1.8		1.9		7.5	1.9		1.8	
Alkalinity, meq/l	17.9					18.4					19.0				
acidity, meq/l		8.6		8.8			8.6		9.2			7.8		9.2	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	197.3	175.6	11.0	156.1	20.9	226.0	212.7	5.9	163.9	27.5	212.5	219.6		181.7	14.5
Chloride, mg Cl/l	86.2	100.0		313.0		68.4	150.0		348.4		82.6	171.2		329.4	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		pink		pink	pink		pink		pink	pink		pink	
Color threshold	1:100	1:100		10:100		1:100	1:100		10:100		1:100	1:100		10:100	
Average light absorption, E	0.412	0.262	36.4	0.172	58.3	0.392	0.328	16.3	0.172	56.1	0.406	0.312	23.1	0.199	51.0

Table 10-43 (con.)

	Average sample from a 4-h, 30-min cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.9	2.4		2.3	
Alkalinity, mval/l	18.0				
Acidity, mval/l		7.2		6.4	
Permanganate COD, mg O_2/l	60.5	52.5	13.2	40.0	33.9
BOD_5, mg O_2/l	17.5	0.8	95.4	0.5	97.1
Dichromate COD, mg O_2/l	212.5	195.0	8.2	143.2	32.6
Chloride, mg Cl/l	78.1	106.5		323.0	
Anionic detergents, mg/l	0.72	0.76		0.28	61.1
Nonionic detergents, mg/l	26.0	26.0	0.0	19.4	25.4
Color, mg Pt/l	pink	pink		pink	
Color threshold	1:100	1:100		10:100	
Average light absorption, E	0.393	0.097	75.3	0.050	87.3

Table 10-44. The effectiveness of the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP) at a bed loading of 18 BV/h

25 series

	After 45 min					After 1 h, 30 min					After 2 h, 15 min				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.5	1.8		1.8		7.6	2.0		1.9		7.6	1.9		1.9	
Alkalinity, meq/l	20.4					20.2					19.0				
acidity, meq/l		8.4		8.8			9.2		9.0			10.0		9.6	
Permanganate COD, mg O_2/l															
BOD_5, mg O_2/l															
Dichromate COD, mg O_2/l	274.8	195.0	29.0	117.4	57.3	283.6	186.1	34.4	155.1	45.3	255.5	230.5	9.8	163.9	35.9
Chloride, mg Cl/l	51.1	107.1		376.8		72.0	114.2		355.6		75.5	121.3		355.6	
Anionic detergents, mg/l															
Nonionic detergents, mg/l															
Color, mg Pt/l	pink	pink		40.0		pink	pink		40.0		pink	pink		40.0	
Color threshold	5:100	10:100		25:100		5:100	10:100		25:100		4:100	8:100		25:100	
Average light absorption, E	0.409	0.124	69.7	0.039	90.5	0.400	0.237	40.8	0.060	85.0	0.337	0.217	35.6	0.048	85.8

Table 10-44 (con.)

	After 3 h					After 3 h, 45 min					Average sample from 3-h, 15-min cycle				
	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %	Influent	After cationic resin	Removal, %	After anionic resin	Removal, %
pH	7.6	2.0		2.0		7.9	2.0		1.9		7.0	2.4		2.3	
Alkalinity, meq/l	19.6					19.0					19.0				
acidity, meq/l		9.8		9.2			9.4		9.2			9.8		9.2	
Permanganate COD, mg O_2/l											34.0	29.0	14.7	21.0	38.2
BOD_5, mg O_2/l											21.0	0.4	98.1	0.2	99.0
Dichromate COD, mg O_2/l	225.5	210.5	6.7	199.4	11.6	252.6	238.3	5.7	198.4	21.5	274.8	212.5	22.7	161.8	41.1
Chloride, mg Cl/l	72.0	128.4		361.4		79.1	135.5		361.4		78.1	71.0	9.1	375.3	
Anionic detergents, mg/l											2.28	2.52		0.73	68.0
Nonionic detergents, mg/l											52.0	52.0	0.0	38.5	26.0
Color, mg Pt/l	pink	pink		40.0		pink	pink		50.0		pink	pink		50.0	
Color threshold	4:100	7:100		25:100		4:100	5:100		20:100		4:100	5:100		20:100	
Average light absorption, E	0.383	0.246	35.8	0.150	60.8	0.361	0.248	31.3	0.182	49.6	0.377	0.198	47.5	0.083	78.0

Table 10-45. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401), at a bed loading of 6 BV/h during five successive series

	Removal of contaminants in successive series average data, %										Removal of contaminants in 5 series (average data)	
	I		II		III		IV		V			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	17.6	44.1	5.1	53.8	6.2	64.6	23.1	48.7	22.7	59.1	15.3	54.1
BOD_5	90.9	94.5	92.0	92.0	94.8	93.0	94.0	92.0	94.4	94.4	93.2	93.2
Dichromate COD	17.1	41.4	29.8	48.8	8.1	48.8	37.5	60.0	16.0	32.0	21.7	46.2
Anionic detergents	0.0	100.0	0.0	100.0	0.0	97.4	0.0	88.5	0.0	95.7	0.0	96.3
Nonionic detergents	7.7	53.8	6.6	52.5	32.4	62.0	28.4	65.7	20.5	59.1	19.1	58.6
Color, PT scale	40.0	85.0	33.3	83.3	40.0	80.0	33.3	66.6	0.0	60.0	36.6	75.0
Average light absorption, E	51.0	100.0	67.8	88.5	53.0	86.8	37.0	70.9	43.9	71.8	50.5	83.6

Table 10-46. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401) at a bed loading of 12 BV/h during five successive series

	Removal of contaminants in successive series average data, %										Removal of contaminants in 5 series (average data)	
	I		II		III		IV		V			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	12.5	55.4	19.7	55.7	11.8	43.1	12.7	47.0	6.8	13.6	12.7	44.9
BOD_5	95.8	97.9	94.3	95.4	88.9	97.8	96.6	96.6	94.3	96.6	94.0	96.9
Dichromate COD	0.0	12.5	20.7	39.1	5.6	44.9	11.2	29.2	14.0	20.7	10.3	29.3
Anionic detergents	0.0	98.7	0.0	72.7	0.0	88.5	0.0	66.0	0.0	96.9	0.0	84.6
Nonionic detergents	8.3	38.3	7.1	45.8	18.3	50.6	4.9	42.3	20.9	37.2	11.9	42.8
Color, Pt scale	pink	light pink	pink	light pink	pink	light pink	pink	light pink	40.0	70.0	-	-
Average light absorption E	35.7	81.5	19.7	79.0	20.0	71.4	23.7	73.6	44.3	67.0	28.7	74.5

Table 10-47. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Amberlite IRA-401), at a bed loading of 18 BV/h during three successive series

	Removal of contaminants in successive series average data, %						Removal of contaminants in 3 series (average data)	
	I		II		III			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	1.6	46.9	10.3	38.2	4.6	32.3	5.5	39.1
BOD_5	98.3	97.8	98.7	99.1	94.6	96.2	97.2	97.7
Dichromate COD	5.8	22.7	7.5	28.8	7.7	29.5	7.0	27.0
Anionic detergents	0.0	88.0	0.0	62.5	0.0	98.1	0.0	82.9
Nonionic detergents	7.3	46.1	3.4	47.1	0.0	46.6	3.6	46.6
Color, Pt scale	pink	light pink	brown	light brown	red	light red		
Average light absorption, E	24.0	76.8	52.3	94.0	43.6	92.1	40.0	87.6

Table 10-48. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 6 BV/h during three successive series

	Removal of contaminants in successive series average data, %						Removal of contaminants in 3 series (average data)	
	I		II		III			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	23.5	50.0	22.8	40.4	1.3	31.6	15.9	40.7
BOD_5	89.6	91.3	90.0	94.0	96.3	97.0	92.0	94.1
Dichromate COD	29.0	43.5	8.4	33.4	15.7	47.1	17.7	41.3
Anionic detergents	0.0	80.0	0.0	48.1	0.0	67.1	0.0	65.1
Nonionic detergents	9.6	38.5	18.2	42.9	11.9	51.9	13.2	44.4
Color, Pt scale	light red	0.0	light red	0.0	light brown	0.0	-	-
Average light absorption, E	53.6	90.6	39.5	76.7	53.5	79.2	48.9	82.2

Table 10-49. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 12 BV/h during three successive series

	Removal of contaminants in successive series average data, %						Removal of contaminants in 3 series (average data)	
	I		II		III			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	0.0	10.0	8.2	19.7	0.0	30.9	2.7	20.2
BOD_5	94.7	94.0	97.3	96.0	97.8	98.3	96.6	96.1
Dichromate COD	10.3	19.2	7.7	25.3	1.6	40.8	6.5	28.4
Anionic detergents	0.0	65.4	0.0	41.8	0.0	67.4	0.0	58.2
Nonionic detergents	4.1	40.8	14.9	28.1	9.0	58.8	9.3	42.6
Color Pt scale	16.7	50.9	14.3	58.3	light pink	0.0	-	-
Average light absorption, E	49.2	77.5	51.1	78.8	0.9	89.2	33.7	81.8

Table 10-50. Average contaminant removal values in the dual ion-exchange process with cationic and anionic resins (Zeolite 325 and Zeolite KMP), at a bed loading of 18 BV/h during three successive series

	Removal of contaminants in successive series average data, %						Removal of contaminants in 3 series (average data)	
	I		II		III			
	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin	After cationic resin	After anionic resin
Permanganate COD	26.7	44.4	13.2	33.9	14.7	38.2	18.2	38.8
BOD_5	98.6	98.6	95.4	97.1	98.1	99.0	97.4	98.2
Dichromate COD	23.4	39.2	8.2	32.6	22.7	41.1	18.1	37.6
Anionic detergents	0.0	73.8	0.0	61.1	0.0	68.0	0.0	67.6
Nonionic detergents	0.7	28.3	0.0	25.4	0.0	26.0	0.2	26.6
Color, Pt scale	light pink	0.0	light pink	0.0	light pink	0.0	-	-
Average light absorption, E	24.8	59.1	75.3	87.3	47.5	78.0	49.2	74.8

Table 10-51. Average values of pollutant removal for cation Zeolite 325 and anion Amberlite IRA-401 dual systems

Specifications	Series 4-8 bed loading 6 BV/h		Series 9-13 bed loading 12 BV/h		Series 14-16 bed loading 18 BV/h	
	After cation	After anion	After cation	After anion	After cation	After anion
Permanganate COD %	15.3	54.1	12.7	44.9	5.5	39.1
Dichromate COD %	21.7	46.2	10.3	29.3	7.0	27.0
Anionic detergents %	0.0	96.3	0.0	84.6	0.0	82.9
Nonionic detergents %	19.1	58.6	11.9	42.8	3.6	46.6
Spectrophotometric color %	50.5	83.6	28.7	74.5	40.0	87.6

Table 10-52. Average values of pollutant removal for the cation Zeolite 325 and the anion Zeolite KMP system

Specifications	Series 17-19 bed loading 6 BV/h		Series 20-22 bed loading 12 BV/h		Series 23-25 bed loading 18 BV/h	
	After cation	After anion	After cation	After anion	After cation	After anion
Permanganate COD %	15.9	40.7	2.7	20.2	18.2	38.8
Dichromate COD %	17.7	41.3	6.5	28.4	18.1	37.6
Anionic detergents %	0.0	65.1	0.0	58.2	0.0	67.6
Nonionic detergents %	13.2	44.4	9.3	42.6	0.2	26.6
Spectrophotometric color %	48.9	82.2	33.7	81.8	49.2	74.8

SECTION 11

HYPERFILTRATION PROCESS

INTRODUCTION

The present trend in wastewater treatment requires the application of treatment processes that provide recycling possibilities. One of the modern industrial wastewater reclamation techniques is the hyperfiltration (reverse osmosis) process, which yields pure product water (permeate) and concentrated residue. Hyperfiltration is a membrane separation process useful for separation of dissolved substances from the wastewater. It is successfully used for desalination of water and for industrial applications such as textile finishing plants [78], where the products or chemicals recovered are of significant value. Application of the hyperfiltration process for tertiary treatment of municipal wastewater appeared to be too expensive in comparison with other techniques [79]. This part of the project was carried out to evaluate the membrane performance and the feasibility of the hyperfiltration process for mixed municipal and textile wastewater treatment. Hyperfiltration equipment was installed at the pilot plant in Andrychow.

PILOT PLANT EQUIPMENT

Pretreatment Installation

The research equipment consisted of a pretreatment plant and a hyperfiltration plant (figure 11-1). The pretreatment process included upflow contact filtration with an alum dosage of 10 mg/l and 1 mg/l of polyelectrolyte; two-stage, dual media, anthracite-sand filtration; and pH control between the filters. All the filters were made of Plexiglas tubes 15 cm in diameter and differing in height; 3.0 m of upflow contact filters and 2.0 m of anthracite-filters were included. The granulations of the filter beds were as follows:

1. Upflow contact filter (beginning from the top of the bed):
   - 25 cm sand 1.0 to 1.5 mm,
   - 150 cm gravel 1.5 to 2.5 mm, and
   - 25 cm gravel 5 to 15 mm;
2. First-stage anthracite-sand filter (beginning from the top of the bed):
   - 50 cm anthracite 0.75 to 1.2 mm,
   - 50 cm sand 0.5 to 0.75 mm, and
   - 15 cm gravel 1 to 10 mm;

3. Second-stage anthracite-sand filter (beginning from the top of the bed):

   - 25 cm anthracite 0.5 to 0.75 mm,
   - 50 cm sand 0.2 to 0.5 mm,
   - 15 cm sand 0.75 to 1.0 mm, and
   - 15 cm gravel 1 to 10 mm.

The filtration rate for all filters was kept within the range of 6.8 to 10 m^3/m^2h, depending on the capacity of the hyperfiltration installation. The average filter run was about 12 h for upflow contact filtration and about 8 h for anthracite-sand filtration. The pH was controlled to meet the membrane requirements and was kept at the average level of 5.5 with variations in the range of 3.0 to 6.9. The pretreatment performance is shown in table 11-4. The porcelain cartridge filter (1.31 m^2 in area) was not in use because clogging rendered its operation unsatisfactory. The average run of this filter was about 30 min.

Hyperfiltration Installation

The pretreated wastewater was collected in the 2-m^3 stainless steel elevated storage tanks. The membrane was evaluated in a pressure loop in which a P-1QCA 2.4-m^3/h Sunflo pump with 7.4-kW (10hp) motor was employed. Since temperature control was required, the pressure loop included a double-pipe heat exchanger. All the pipings, joints, valves, etc., shown in figure 11-1 were made of stainless steel 1H18N9T (Polish Standard) equal to 316 SS (American Standard).

The following measuring instruments were included: a pH meter, a 12-point temperature recorder, two flowmeters with recorders, a pressure gage, and a pressure gage with recorder. The measuring points are shown in figure 11-1. A multichannel metering pump was employed to collect the samples.

PROCESS PERFORMANCE

The initial investigation program included evaluation of dynamically formed $Zr_{IV}O$ PAA and cellulose acetate spiral wound membranes. Both membrane modules were preliminarily tested on the 0.1 M salt solution. The data from these tests are shown in tables 11-1 and 11-2. Since the cellulose acetate spiral wound membrane (module model ROGA 4160 S) worked satisfactorily giving aliquot rejection and stable flux, it was chosen for further investigation. During the salt solution test and during the first day of the 4-d test, the installation worked with full concentrate recirculation in the system. After the first approximately 24 h of the test, constant discharge of the concentrate, amounting to 90 percent water recovery, was conducted. During the whole test the installation was fed with a controlled amount of pretreated wastewater to insure constant wastewater volume in the system. During the last approximately 48 h of the test, discharge of the concentrate was controlled so as to achieve 50 percent product water recovery.

The test of hyperfiltration was terminated by the failure of the membrane module. After 94 h, a loss of power caused a second shutdown of the hyperfiltration test unit. This shutdown lasted 5 d because of bulking of the activated sludge process. The module was flushed with clean water and stored with 0.5 percent formaldehyde during this period. After 5 d, startup of the hyperfiltration unit was cancelled because the initial permeate flow was 6 l/min (250 percent of the rated capacity for clean water) and the rejections were 0 percent.

Physical inspection of the module revealed that the flow passages were partially blocked by sludge. The membrane spiral was telescoped about 5 m in the direction of flow. Even though no large pressure drop across the module was observed, the membrane displacement indicates that a pressure differential existed, at least momentarily, during startup. The presence of fine particles in the feed resulted in the formation of a fouling layer on the membrane surface, causing a flux decline. Any stoppage of the feed flow rate may permit particle settling and a more rapid buildup of the deposited layer. The long duration (5 d) perhaps allowed all the particles to settle and also to form a compacted layer and essential plugging of the flow passage. Subsequent startup could place a full pumphead pressure differential across the module unless a flow bypass is provided.

The operating conditions of the ROGA module are shown in table 11-3 and figure 11-2. Chemical composition of concentrate and product water is given in table 11-4. Color analyses of the treated wastewater and concentrate are shown in figures 11-3 through 11-6.

COLLECTION AND STORAGE OF SAMPLES

As already mentioned, a multichanneled metering pump was employed to collect daily average composite samples. Since samples were analyzed up to 10 d after collection, it was necessary to store them at about 5° C. Membrane performance was checked every hour by means of pH and conductivity measurements.

DISCUSSION OF RESULTS AND CONCLUSIONS

The color rejection during the test was approximately 99 percent, while the conductivity rejection varied from 97 percent at the beginning to 89 percent at the end of investigations. These numbers are comparable to those obtained by Brandon and Porter for the isolated wastewater from textile dyeing and finishing processes [79].

The pretreatment process used for the hyperfiltration investigation was not satisfactory. For further investigations, use of more efficient filtration will be necessary. Based on chemical analysis given in table 11-4, compared with the data presented in reference [79], it can be asserted that the membrane performance is satisfactory for water reuse for the textile industry. Concentrations of dissolved solids, COD, turbidity, and other constituents in product water obtained (table 11-4) are much lower than those given in table 10, reference [79] for product water reused in textile processes. This finding is confirmed by Brandon, Sargent, and Samfield [81].

The permeate flow sharply decreased from 2.4 l/min at the beginning of the test, and it reached the stable range of 0.9 l/min over the last 48 h of the test. Thus, 0.9 l/min might be regarded as a design membrane capacity for ROGA module model 4160 S, even though this was only a test.

The use of a better pretreatment process may prevent flux decline due to fouling. It is also essential to prevent membrane module plugging.

It is absolutely necessary to wash the membrane at least with plain water during every break in the process. It is advisable to fill the module with 0.5 percent formaldehyde water solution under the elevated pressure as prescribed by the manufacturer. This applies to short breaks as well.

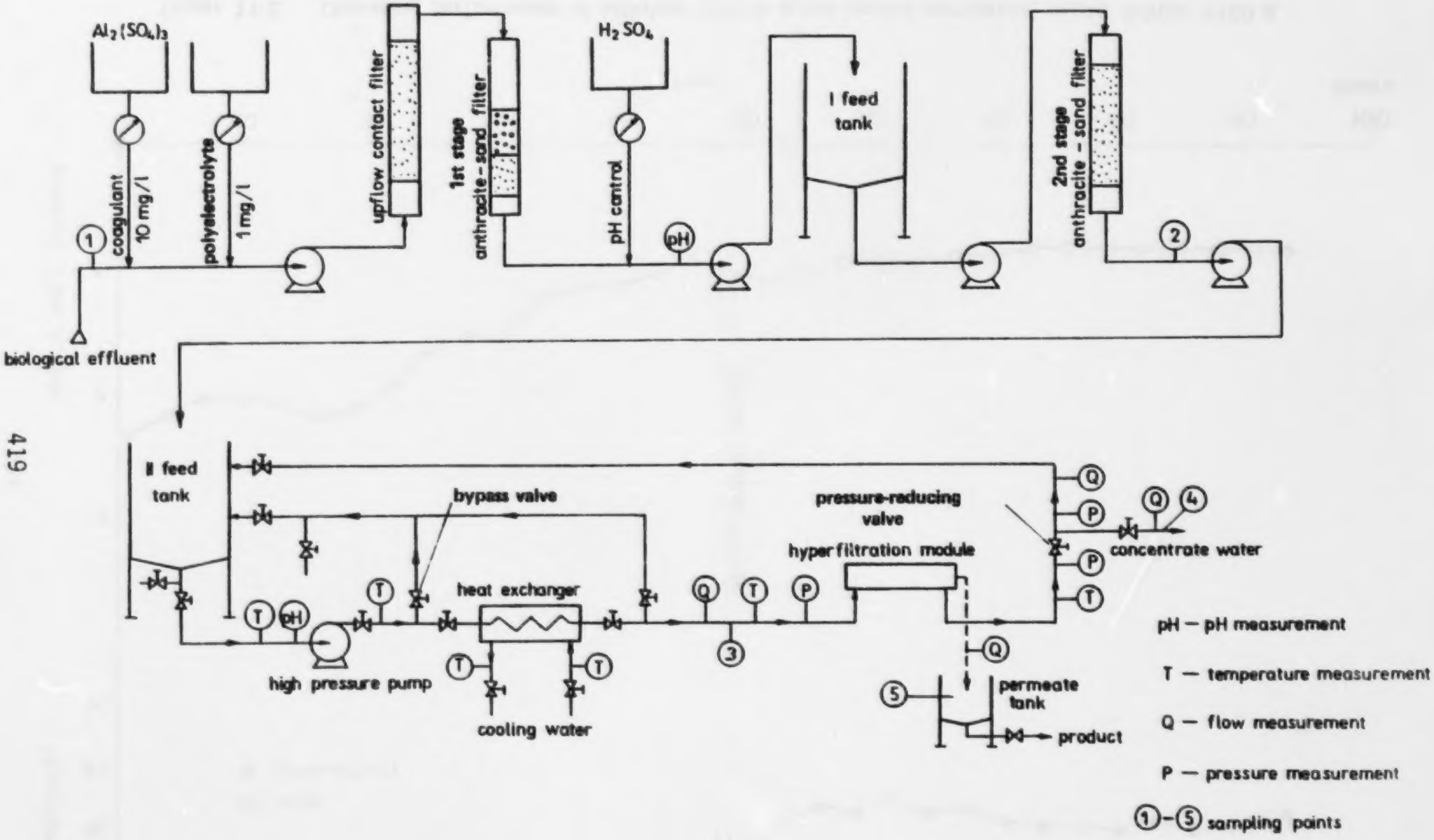

$Al_2(SO_4)_3$
coagulant
10 mg/l
polyelectrolyte
1 mg/l
①
biological effluent
upflow contact filter
1st stage
anthracite - sand filter
H_2SO_4
pH control
pH
I feed
tank
2nd stage
anthracite - sand filter
②
II feed
tank
bypass valve
heat exchanger
T
pH
high pressure pump
cooling water
Q
T
P
③
pressure-reducing
valve
hyperfiltration module
Q
P
P
T
Q
④
concentrate water
Q
⑤
permeate
tank
product
pH — pH measurement
T — temperature measurement
Q — flow measurement
P — pressure measurement
①-⑤ sampling points

Figure 11-1. Schematic diagram of pilot plant at Andrychow for investigation of hyperfiltration process.

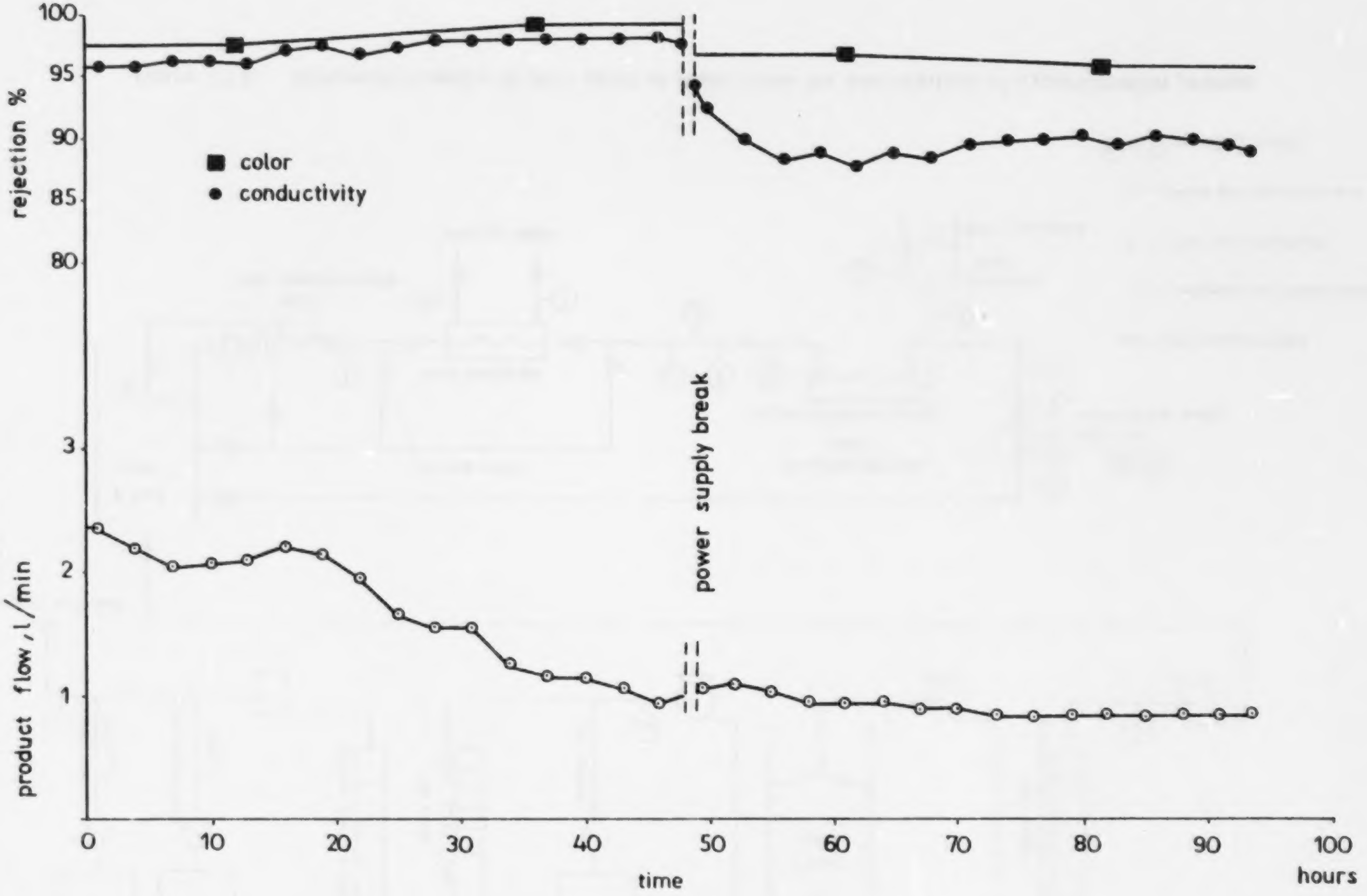


Figure 11-2. **Operating performance of cellulose acetate spiral wound membrane, model ROGA 4160 S.**

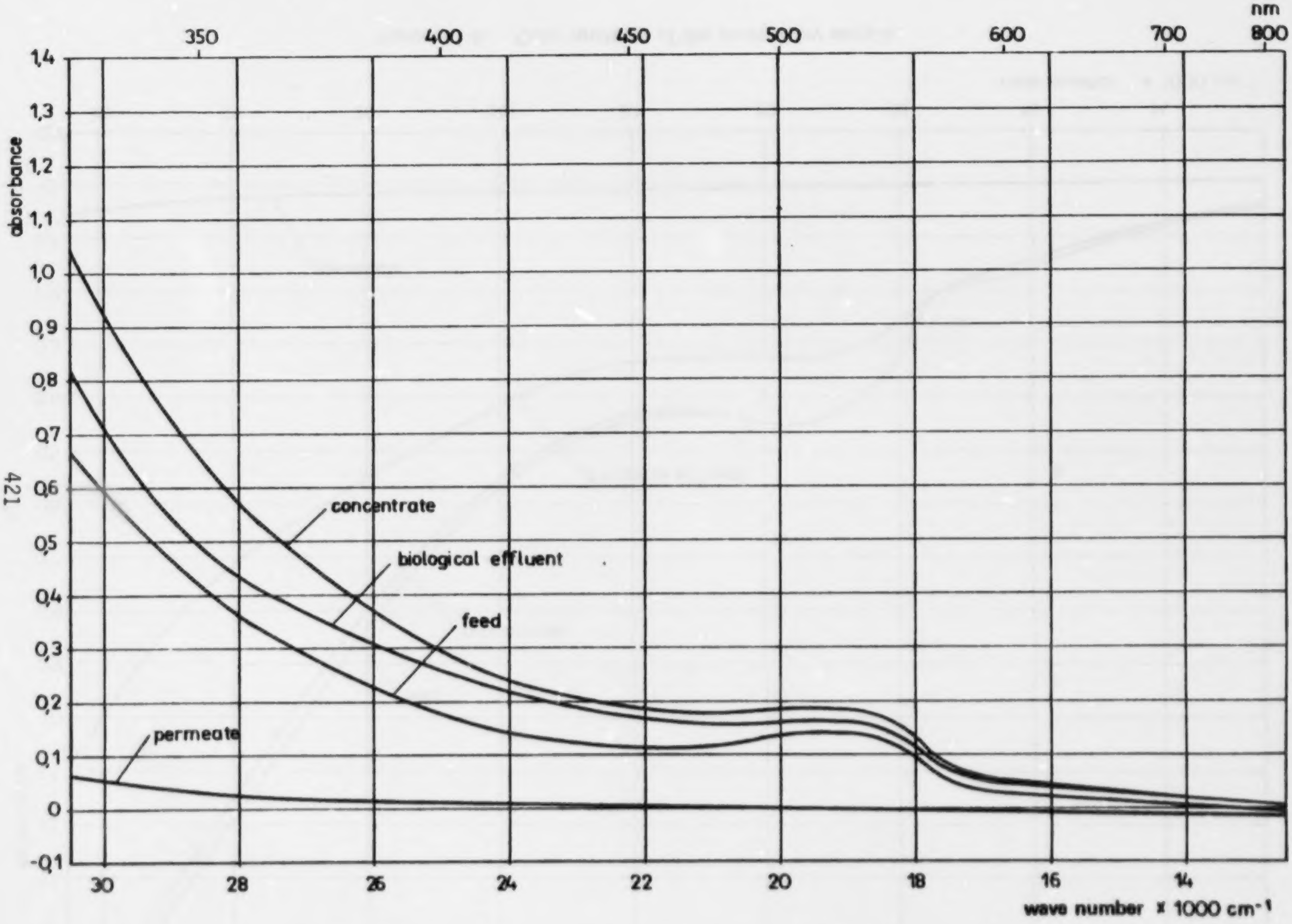


Figure 11-3. Color analyses of the first day sample.

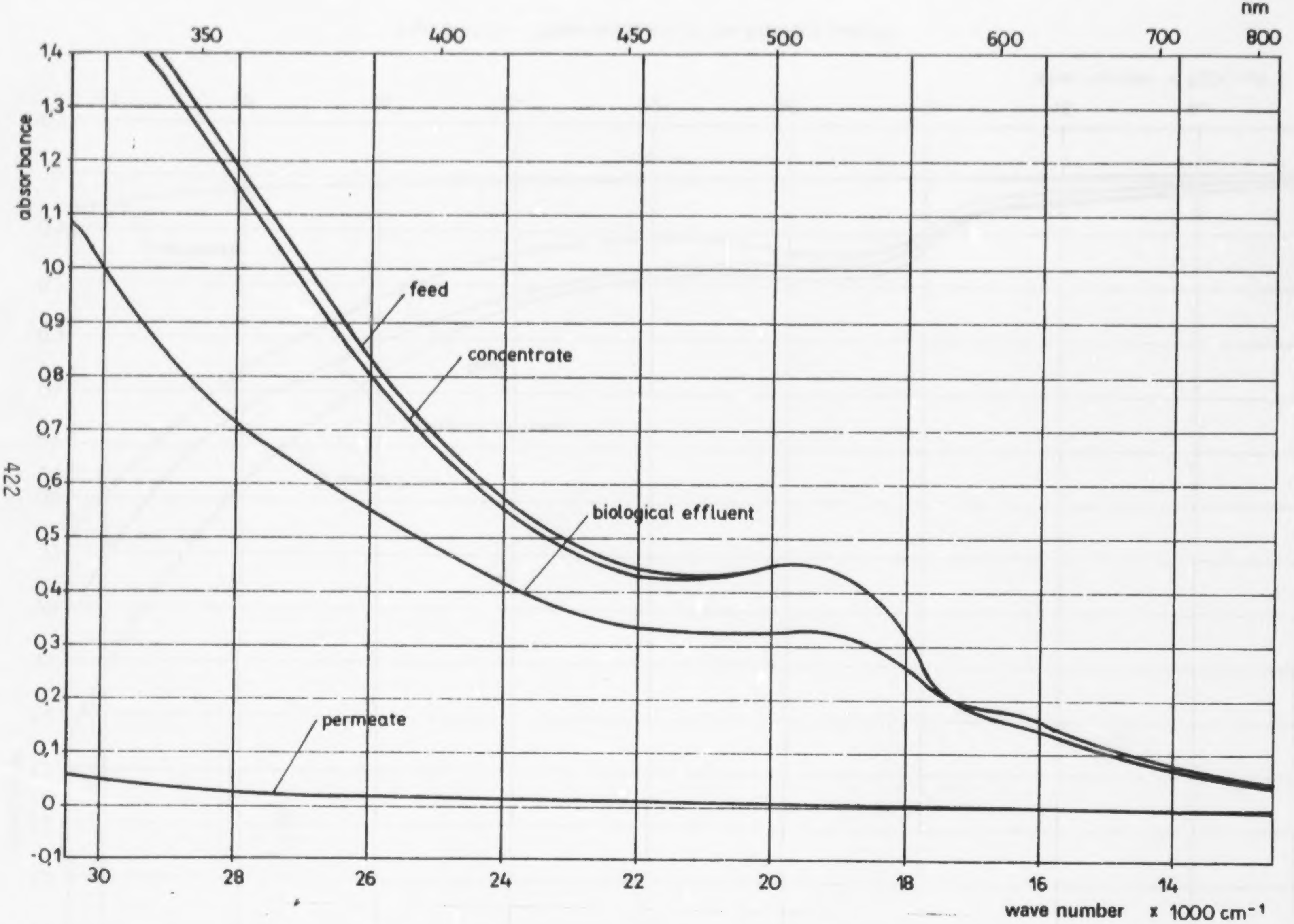


Figure 11-4. Color analyses of the second day sample.

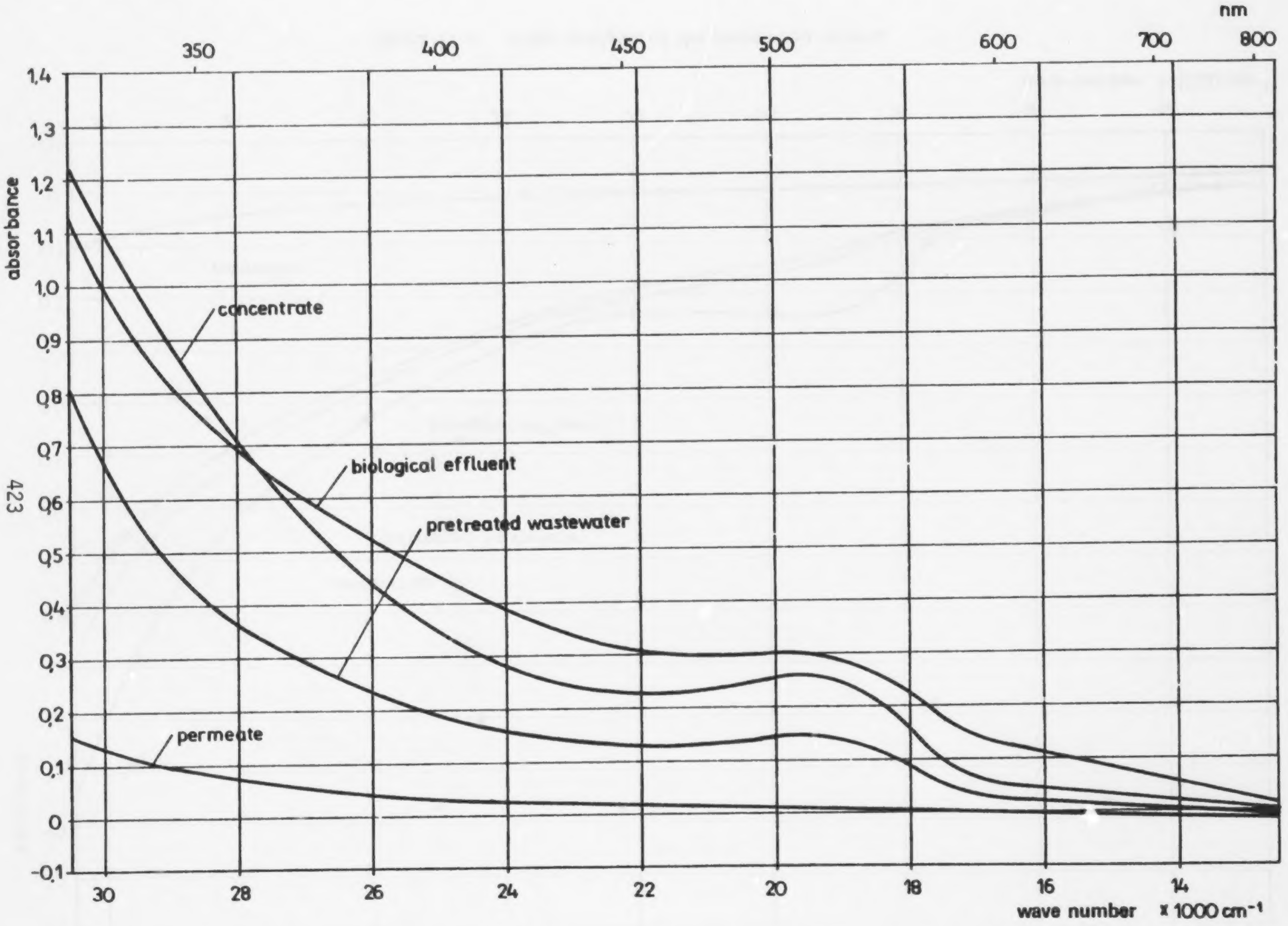


Figure 11-5. Color analyses of the third day sample.

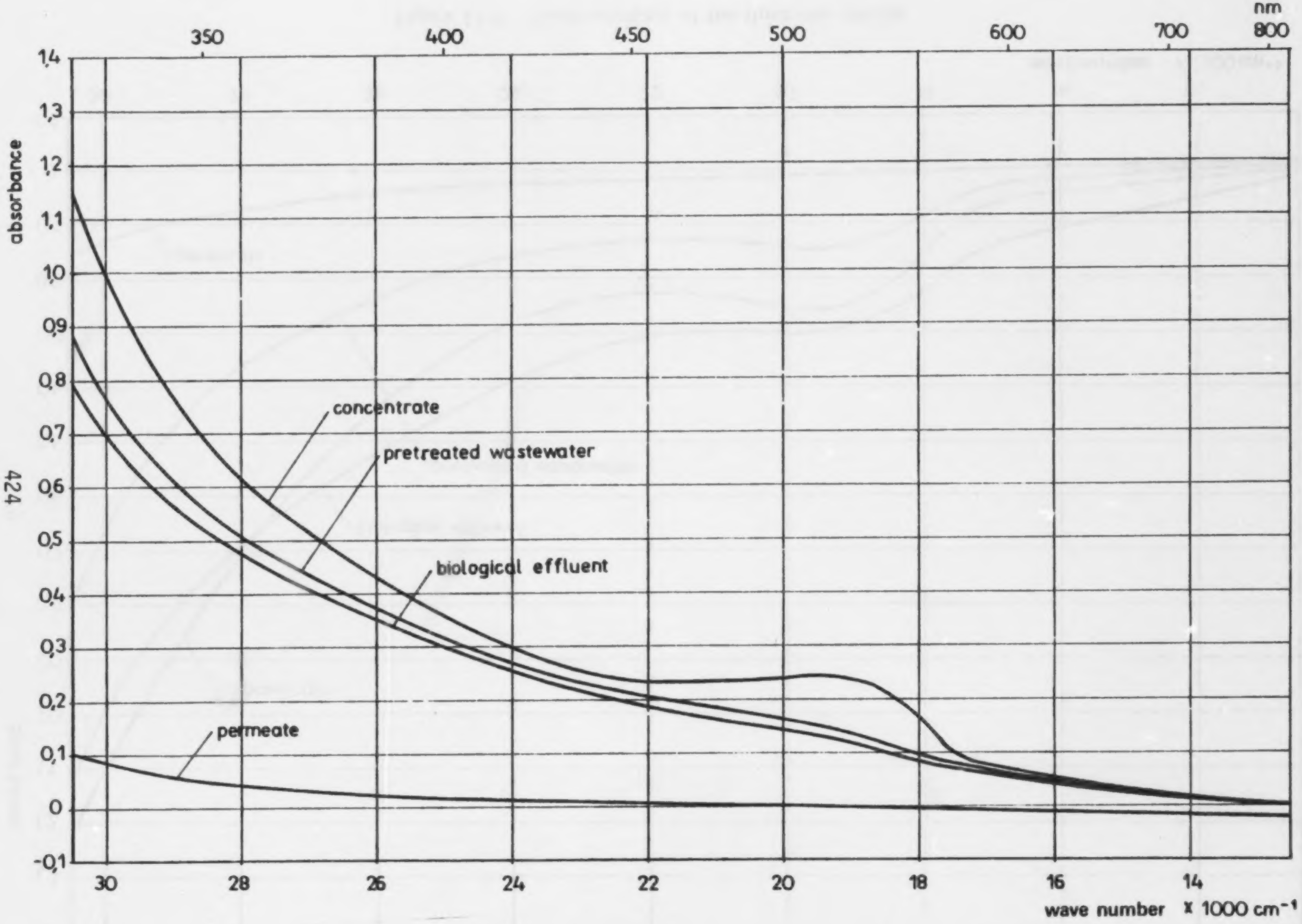


Figure 11-6. Color analyses of the fourth day sample.

Table 11-1. Preliminary test for ROGA membrane using 0.1 mol salt solution

			Pressure	Feed					Permeate					
No.	Date	Hour	at	Flow l/min	Temp. °C	pH -	Cond. uS·cm-1	Chloride ions mg/l Cl$^-$	Flow l/min	pH -	Cond. uS·cm-1	Chloride ions mg/l Cl$^-$	% conductivity rejection	% chloride ions rejection
1	5/27/77	13.00	25.0	43.3	20	7.3	2133	728	2.56	7.0	129	53	94.0	92.7
2		14.00	25.0	43.3	22	5.9	2252	852	2.80	5.5	148	53	93.4	93.8
3		15.00	25.0	40.8	21	5.5	2568	905	2.64	5.7	154	55	94.0	93.9
4		16.00	25.0	40.8	20	6.3	2963	970	2.47	5.5	183	60	93.8	93.8
5		17.00	25.5	41.7	19.5	6.6	3239	1135	2.50	5.5	205	62	93.7	94.5
6		18.00	25.5	41.2	19.5	6.4	3713	1335	2.45	5.9	229	78	93.8	94.2
7		19.00	25.0	40.8	19.5	6.9	4661	1608	2.42	5.8	296	100	93.6	93.8
8		20.00	25.0	41.2	19.5	7.0	5846	1980	2.43	6.0	367	114	93.7	94.2

Note: Module contained 65 ft^2 (6.04m^2) of membrane area.

Table 11-2. Preliminary test for dynamically formed membrane using mol salt solution

			Feed						Permeate						
No.	Date	Hour	Pressure at	Flow l/min	Temp. °C	pH -	Cond. uS·cm^{-1}	Chloride ions mg/l Cl$^-$	Flow l/min	pH -	Cond. uS·cm^{-1}	Chloride ions mg/l Cl$^-$	Flux l/m^2·h	% conductivity rejection	% chloride ions rejection
1	5/27/77	12.00	30.0	44.2	18	7.0	1738	-	0.035	7.1	790	-	39.6	54.5	-
2		13.00	30.5	44.2	18	7.0	1778	692	0.035	6.9	687	195	39.6	61.3	71.8
3		14.00	30.5	44.2	19	7.0	1817	1012	0.035	7.3	695	284	39.6	61.7	71.9
4		15.00	30.5	44.2	19	7.0	1817	657	0.037	6.7	711	266	41.9	60.9	59.5
5		16.00	30.5	44.2	19	7.2	1896	657	0.032	6.9	695	266	36.2	63.3	59.5
6		17.00	30.5	44.2	19	7.0	1912	675	0.033	6.9	711	266	37.4	62.8	60.5
7		18.00	30.5	44.2	19	6.9	1912	621	0.032	6.9	711	266	36.2	62.8	57.1
8		19.00	30.5	44.5	20	7.2	1833	621	0.036	7.0	679	266	40.8	62.9	57.1
9		20.00	30.5	44.5	21	7.0	2007	621	0.037	7.2	695	284	41.9	65.4	54.3
10		21.00	30.5	44.5	22	7.2	1975	657	0.040	7.0	727	266	45.3	63.2	59.5
11		22.00	30.5	44.5	22	7.2	1959	639	0.041	7.1	743	266	46.4	62.1	58.7
12		23.00	30.5	44.5	23	7.0	2038	621	0.042	6.9	719	284	47.5	64.7	54.3
13		24.00	30.5	44.5	24	7.1	2015	639	0.043	6.9	735	284	48.7	63.5	55.6
14	5/26/77	1.00	30.5	44.3	24	7.2	1991	646	0.044	6.9	727	273	49.8	63.5	57.7
15		2.00	30.5	44.2	25	7.1	2109	781	0.045	7.0	766	373	50.9	63.7	52.3
16		3.00	30.5	44.2	25	7.1	2157	657	0.045	7.1	766	337	50.9	64.5	48.6
17		4.00	30.5	44.2	25	7.1	2220	763	0.046	6.9	766	320	52.1	65.5	58.1
18		5.00	30.5	44.2	25	7.2	2173	763	0.046	6.9	766	337	52.1	64.5	55.8
19		6.00	30.5	44.2	26	7.1	2133	657	0.046	6.9	758	337	52.1	64.4	48.7
20		7.00	30.5	44.2	26	7.1	2157	692	0.047	6.9	766	284	53.2	64.5	59.0
21		8.00	30.5	44.2	26	7.1	1631	675	0.047	7.0	766	337	53.2	53.0	50.0
22		9.00	30.5	44.2	22	7.2	2015	675	0.037	6.9	711	320	41.9	64.7	52.6
23		10.00	30.5	44.2	22	7.0	1959	621	0.037	7.0	695	266	41.9	64.5	57.1

Note: Module contained 0.57 ft^2 (0.53m^2) of membrane area.

Table 11-3. Operating conditions of the spiral wound cellulose acetate module (model ROGA 4160 S) during the wastewater test

			Concentrate				Product water			
Operating time (h)	Pressure (at)	Feed dm³/h	Flow dm³/h	Temp. °C	pH -	Cond. µS·cm⁻¹	Flow dm³/h	pH -	Cond. µS·cm⁻¹	Conductivity rejection (%)
1	25	2400	0.0	22	6.0	980	144	5.5	45	95.4
2	25	2400	0.0	22	6.4	1043	138	5.7	40	96.1
3	25	2400	0.0	22	6.6	1185	138	5.7	47	96.0
4	25	2400	0.0	22	6.3	1142	132	5.6	62	95.6
5	25	2400	0.0	22	5.1	1620	126	5.3	68	95.8
6	25	2400	0.0	22	4.7	1778	123	5.1	73	95.8
7	25	2400	0.0	21	5.3	1888	123	5.9	64	96.6
8	25	2400	0.0	21	6.0	2109	126	5.8	70	96.7
9	25	2400	0.0	21	6.1	2212	126	5.9	70	96.8
10	25	2400	0.0	21	6.2	2331	123	5.9	71	97.0
11	25	2400	0.0	21	4.3	2726	120	4.8	140	94.9
12	25	2400	0.0	23	4.0	3160	120	4.8	132	95.8
13	25	2400	0.0	24	4.0	3160	126	4.9	130	95.8
14	25	2350	0.0	23	4.1	3200	132	5.0	100	96.9
15	25	2350	0.0	24	4.7	3207	132	5.6	88	97.2
16	25	2350	0.0	26	5.5	3081	132	5.8	86	97.2
17	25	2350	0.0	25	5.8	3310	132	5.8	92	97.2
18	25	2350	0.0	26	6.1	3389	132	5.8	94	97.2
19	25	2350	0.0	26	6.4	3460	132	6.0	93	97.3
20	25	2350	0.0	26	6.5	3468	126	6.1	92	97.3
21	25	2350	0.0	26	6.5	3650	126	6.2	125	96.6
22	25	2350	0.0	25	6.4	3674	114	6.1	122	96.7
23	25	2350	0.0	24	6.5	3571	108	6.2	113	96.8
24	25	2350	0.0	23	6.4	3713	103	6.1	115	96.9
25	25	2350	0.0	22	6.4	3713	99	6.0	98	97.4
26	25	2350	10.5	23	6.4	3784	99	6.0	94	97.4
27	25	2400	10.5	23	6.5	4029	84	6.0	96	97.6
28	25	2400	10.5	24	6.6	4345	98	6.0	93	97.8
29	25	2400	10.5	24	6.6	4345	95	5.9	98	97.7
30	25	2400	10.5	25	6.7	4503	95	5.6	103	97.7

Table 11-3 (con.)

Operating time (h)	Pressure (at)	Feed dm³/h	Concentrate Flow dm³/h	Temp. °C	pH -	Cond. µS·cm⁻¹	Product water Flow dm³/h	pH -	Cond. µS·cm⁻¹	Conductivity rejection (%)
31	25	2400	10.5	25	6.6	4510	92	5.8	103	97.7
32	25	2400	10.5	25	6.5	4526	90	5.7	109	97.6
33	25	2400	10.5	25	6.6	4345	78	5.9	111	97.4
34	25	2400	8.4	25	6.5	4515	72	5.8	105	97.7
35	25	2400	8.4	25	6.5	4622	72	5.8	106	97.7
36	25	2400	8.2	25	6.6	4582	71	5.6	104	97.7
37	25	2400	8.2	25	6.8	4661	69	5.8	109	97.7
38	25	2400	7.6	26	6.9	4740	69	5.8	104	97.8
39	25	2400	7.6	27	6.6	4898	76	6.0	105	97.9
40	25	2400	7.6	25	6.5	4898	71	6.2	113	97.7
41	25	2400	7.6	25	6.4	4977	67	6.1	107	97.9
42	25	2350	7.3	25	6.3	5056	64	6.3	117	97.7
43	25	2370	6.7	25	6.0	5056	62	6.0	109	97.8
44	25	2350	6.7	25	6.5	5293	60	6.0	103	98.1
45	25	2350	6.7	25	6.0	5293	61	6.0	101	98.1
46	25	2370	6.7	25	6.0	5530	59	5.5	137	97.5
47	25	2370	6.3	24	6.0	5688	56	6.0	135	97.6
48	25	2360	5.3	24	6.0	5688	48	6.0	144	97.5
49	25	2300	8.0	23	4.5	6715	72	4.0	418	93.8
50	25	2330	7.3	23	4.0	6952	66	5.0	521	92.5
51	25	2320	7.3	24	4.0	6557	66	5.0	656	90.0
52	25	2320	7.3	24	4.0	5767	66	5.0	585	89.9
53	25	2300	70.0	24	4.0	5846	66	5.0	608	89.6
54	25	2300	66.0	24	4.5	5688	66	5.5	600	89.5
55	25	2300	65.0	23	4.5	4487	63	6.0	634	85.9
56	25	2350	60.0	23	4.5	5293	60	6.0	553	89.6
57	25	2350	60.0	23	4.5	5925	60	5.0	695	88.3
58	25	2360	60.0	23	4.0	5767	58	6.0	687	88.1
59	25	2350	58.0	23	5.5	5609	57	5.5	656	88.3
60	25	2350	58.0	24	5.0	5293	57	5.5	561	89.4

Table 11-3 (con.)

Operating time (h)	Pressure (at)	Feed dm^3/h	Concentrate Flow dm^3/h	Temp. °C	pH -	Cond. µS·cm-1	Product water Flow dm^3/h	pH -	Cond. µS·cm-1	Conductivity rejection (%)
61	25	2350	58.0	23	5.0	5214	57	5.0	656	87.4
62	25	2350	58.0	25	5.0	5530	60	4.5	751	86.4
63	25	2300	58.0	25	5.5	5372	60	5.0	640	88.1
64	25	2300	58.0	24	5.5	5372	55	4.5	585	89.1
65	25	2300	58.0	24	5.0	5214	55	4.0	608	88.3
66	25	2280	55.0	23	4.5	5056	54	4.0	600	88.1
67	25	2300	55.0	24	5.0	4819	54	4.5	672	86.1
68	25	2250	55.0	24	5.0	4740	54	4.5	537	88.7
69	25	2300	55.0	24	4.5	4819	55	4.5	529	89.0
70	25	2300	55.0	24	5.0	4503	55	4.5	482	89.3
71	25	2300	55.0	24	5.0	4582	54	4.5	498	89.1
72	25	2320	54.0	23	4.0	4819	51	4.5	498	89.7
73	25	2320	54.0	23	3.5	4503	51	4.5	474	89.5
74	25	2340	52.0	23	3.5	4503	51	7.5	474	89.5
75	25	2330	52.0	23	4.0	4266	51	6.0	442	89.7
76	25	2330	52.0	23	3.0	4187	51	6.4	419	90.0
77	25	2330	52.0	22	3.3	4187	51	6.5	442	89.4
78	25	2330	54.0	22	4.9	3729	54	6.4	391	89.5
79	25	2320	54.0	22	5.0	3784	55	6.0	371	90.2
80	25	2320	54.0	23	5.5	3634	55	5.8	367	89.9
81	25	2320	54.0	23	5.4	3595	54	5.6	378	89.5
82	25	2320	54.0	22	6.0	3721	54	5.7	403	89.2
83	25	2320	54.0	22	6.1	4029	54	5.8	427	89.4
84	25	2300	54.0	23	6.0	3753	54	5.8	411	89.0
85	25	2320	54.0	23	6.1	3721	53	5.4	356	90.4
86	26	2320	54.0	24	6.6	3737	55	5.6	361	90.3
87	26	2320	54.0	25	6.5	3563	55	5.6	375	89.5
88	26	2300	54.0	26	6.6	3547	56	6.0	367	89.7
89	26	2300	54.0	26	6.7	3555	55	5.8	367	89.5
90	26	2320	54.0	26	6.4	3500	54	5.8	375	89.3
91	26	2320	54.0	27	6.6	3555	56	5.7	379	89.3
92	26	2350	54.0	26	6.5	3279	53	5.6	348	89.4
93	26	2340	54.0	25	6.4	3239	53	5.5	348	89.3
94	26	2350	54.0	24	6.5	3081	51	6.0	347	88.7

Table 11-4. Chemical analysis of the composite samples for entire test period

Constituent	Biological effluent	Pretreated wastewater	Feed water	Concentrate	Product water	Rejection (%)*
Dichromate COD, mg/l	161.56	138.0	211.2	226.8	14.96	92.9
Permanganate COD, mg/l	43.5	34.0	51.1	51.1	5.5	89.3
Dissolved solids, mg/l	1080*	1247	2720	2815	181	93.3
Turbidity-SiO_2, mg/l	10.0	3.0	3.0	4.0	1.0	66.7
Nonionic detergents, mg/l	27.4	16.3	70.5	72.5	0.40	99.4
Anionic detergents, mg/l	2.1	1.7	2.3	2.3	0.50	78.4
Chloride, mg/l	65.7	131.7*	200.6	239.2	16.7	91.7
Sulfate, mg/l	471.1	720.2[†]	1008.2	1068.2	74.5	92.6
Chromium, mg/l	0.0	0.0	0.0	0.0	0.0	--
Zinc, mg/l	0.33	0.26	1.05	1.16	0.18	82.9
Phenol, mg/l	0.0	0.0	0.0	0.0	0.0	--
BOD_5, mg/l	37.8	18.4	22.5	22.7	4.4	80.4

* Rejection related to the feed.

[†] Increase of chlorides and sulfates concentration caused by HCl or H_2SO_4 dosage for pH content.

SECTION 12

COMBINED SYSTEM AND COMPARISON OF PROCESSES

COMBINED SYSTEM OF TERTIARY TREATMENT

In addition to the investigations of individual technological processes described in previous sections, a combined treatment system was examined in order to check the combined operation of selected tertiary processes at the pilot plant. This system included the processes that were both effective and technically and economically feasible, and on the other hand, those that complemented each other for high quality of final effluent.

These combined processes were studied in two periods (figure 5-15). The first period, September to October 1976, involved the system comprised of contact coagulation, filtration, adsorption, and ozone oxidation (figure 5-13). The second period, February to March 1977, was intended to check the effectiveness of adsorption on a wastewater coagulated dose of 100 mg/l of alum (instead of 250 mg/l and without NaOCl). The ozone oxidation was omitted in the second period.

The effectiveness of individual processes of the combined system has been presented in previous sections: section 7, table 7-11, coagulation and filtration; section 8, table 8-10, figures 8-36 and 8-37, adsorption; and section 9, tables 9-16 and 9-17, oxidation with ozone.

The average effectiveness of the combined system in the first period is summarized in tables 12-1 and 12-2. COD removal in the whole system equaled 95 percent. Total removal of nonionic detergents in the whole system was 76 percent.

Percentage removal of color was determined spectrophotometrically in particular processes:

Contact coagulation	46%
Contact coagulation with oxidation with NaOCl and filtration	96%
Adsorption	80%

The adsorption effluent was completely colorless.

Among the other parameters, permanganate COD concentration decreased from 24 mg of O_2/l in biological effluent to approximately 1.2 mg of O_2/l in adsorption effluent. It changed slightly during ozonation. BOD_5 decreased from 3.3 mg of O_2/l after coagulation and filtration to approximately 2.0 mg of O_2/l in effluent from the adsorption process. Anionic detergents were removed to traces. As is clear from these results, the quality of the treated effluent wastewater is very high and meets, for pollutants analyzed, class I water purity standards (appendix C). Ozone oxidation is in this case superfluous. As a result, in the recommended system this process has been omitted.

COMPARISON OF PROCESSES

Feasibility analysis and choice of processes for practical application should be based on a comparison of their technological effectiveness and on capital and operating costs. Partly because of the rather small scale of the pilot plant, and mainly because of difficulties in comparing prices of materials and structures in Polish and U.S. currency, capital and operating costs have not been included here. Instead, the values of the main individual factors that influence the operating costs have been given.

The effectiveness of individual processes applied after biological treatment based on pilot plant data is summarized in table 12-3.

The consumption of chemicals, materials, and water as well as the percentage of wasted volume is presented in table 12-4.

The wastewater pumping head, which influences the cost of energy, and the major energy used for purposes other than pumping are shown in table 12-5.

It is clear from the data summarized in table 12-5 that the greatest chemical consumption occurs in the case of coagulation; however, activated carbon is the most costly material. The greatest energy consumption occurs in the hyperfiltration process, as a result of very high wastewater pumping head. The energy consumption in ozone oxidation is also considerable. In regard to water consumption for the needs of the process, the greatest consumption occurs in ion exchange for regeneration of resins. It reaches 15 percent of total flow capacity. This amount is then discharged to the sewerage system as concentrated spent regenerant and washings. With hyperfiltration the nonusable concentrate (up to 10 percent) is treatable by conventional treatment techniques [80]. Large volumes of sludge that need to be dewatered occur in the coagulation process. The cost of further treatment of concentrates and sludge is an additional important and often decisive factor in the choice of particular processes for practical application.

Table 12-1. Average effectiveness of the combined system for COD

Kind of sample	Concentration mgO_2/l	Removal in unit processes, %	Cumulative removal, %
Biologically	100		
Contact coagulation effluent	40	60	60
After filtration and preliminary oxidation with NaOCl	30	25	70
After adsorption	6	80	94
After ozonation	5	16	95

Table 12-2. Average effectiveness of the combined system for nonionic detergents

Kind of sample	Concentration mg/l	Removal in unit processes, %	Cumulative removal, %
Biologically treated	10		
After contact coagulation, preliminary oxidation, and filtration	5.6	44 44	44 44
After adsorption	3.7	34	63
After ozonation	2.4	35	76

Table 12-3. Effectiveness of individual processes applied after biological treatment

	Removal, %			
Process	COD	Detergents[a]	Color	Others
Filtration (plain)	av. 30	35[b]	up to 45	Susp. solids below 10 mg/l BOD_5: 30 to 75
Coagulation	av. 70	av. 44	av. 96	
Adsorption				
after AS+F	20 to 50	41 to 48[b]	30 to 50	
after AS+C +F[d]	av. 80	31 to 41	av. 80	TOC: 56 to 73
Oxidation by ozone	av. 32	av. 35[e]	av. 67	
Ion exchange	up to 46	up to 58	74 to 87	
Hyperfiltration	93	99	99	Conductivity: 97 to 89

[a] Nonionic detergents.

[b] Anionic detergents.

[c] Contact coagulation with oxidation and filtration.

[d] After activated sludge, coagulation, and filtration.

[e] In ozonation after adsorption.

Table 12-4. Consumption of chemicals and materials and volume of water wasted

Process	Consumption of chemicals and materials per 1 m^3 of treated wastewater	Water consumption or wasted volume in % of treated wastewater
Filtration	0	5
Adsorption	100 g of act. carbon	2 to 3
Coagulation	250 g of alum	7 to 10
	100 g of HCl	(sludge)
	15 g of NaOCl	
Oxidation	50 g of ozone	0
Ion exchange	2.5 g of NaCl	10 to 15
	1.7 g of HCl	(spent
	1 g of resin	regenerant)
Hyperfiltration	10 g of alum	< 10
	1 g of polyelectrolyte	(rejected
	(for prefiltration)	concentrate)

Table 12-5. Energy consumption and wastewater pumping head

Process	Energy consumption other than pumping kWh per 1 m^3	Wastewater pumping head, in
Filtration	Small	4
Adsorption	Small	4
Coagulation	Small	6
Oxidation	1.2	4
Ion exchange	Small	4
Hyperfiltration	Considerable for pretreatment for spiral wound membrane, small for tubular membrane [78]	250

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APPENDIX A

ANALYTICAL PROCEDURE FOR SELECTED CONSTITUENTS

DETERMINATION OF NONIONIC POLYETHOXYLIC SYNTHETIC SURFACE-ACTIVE AGENTS BY COLORIMETRIC METHOD WITH PHOSPHOTUNGSTIC ACID

Principle

Nonionic polyethoxylic surface-active agents are precipitated in the form of a complex compound with phosphotungstic acid and barium chloride or potassium chloride. The tungsten, making up this compound in a solution of concentrated sulfuric acid, forms with hydroquinone, a red-brown coloring. The intensity of color is measured spectrophotometrically at 500 nm.

Procedure

Measure off into a centrifugal test tube 10 ml of sample, or 10 ml of the sample condensed or diluted to such a volume that the nonionic surface-active substance content is 0.02 to 0.25 mg. Add two drops of hydrochloric acid solution 1 + 1.

Combine 1 ml of barium chloride solution, or 1 ml of potassium chloride in the case where more than 200 mg/l of sulfates appear, and 1 ml of phosphotungstic acid solution. Place the sample in boiling water and heat for 15 min. Spin off the sediment in a centrifugal machine for 15 min at a speed of 2,500 to 3,000 r/min. Carefully decant the liquid from above the sediment; add 10 ml of hot distilled water; mix thoroughly; and spin off the sediment again. Repeat the spinning twice. Decant, and add 3 ml of sulfuric acid. Mix, and after the sediment has totally dissolved, add 1 ml of hydroquinone. Mix. Fill a sample to 10 ml with sulfuric acid, and mix; after 15 min, measure the absorption, providing a light path of 1 cm.

DETERMINATION OF PERMANGANATE COD

Principle

A sample of water or sewage is treated with an excess of potassium permanganate solution in an acidified medium at the temperature of boiling water bath. The amount of the oxidant consumed is then estimated by the titrimetric method. The result is calculated from the net equivalence of $KMnO_4$ consumed and is expressed as milligrams of oxygen per liter of the sample.

Procedure

The container with analyzed water or sewage is well shaken and the exact volume of 100 ml of the sample is transferred to a conical flask. For highly contaminated samples, a smaller volume is measured and made up to 100 ml with distilled water. Then, 5 ml of H_2SO_4 (1:2) and 20 ml of 0.01 N $KMnO_4$ are added and the flask is immersed in boiling water bath for 30 min. After removing the flask from the water bath, 20 ml of 0.01 N oxalic acid is added and the solution is titrated with 0.01 N $KMnO_4$ until the first permanent slight pink color appears.

Calculation:

$$\text{mg/l } O_2 = \frac{(a-b) \times F \times 80}{V}$$

where: a = volume (in ml) of 0.01 N $KMnO_4$ required for titration;

b = volume (in ml) of 0.01 N $KMnO_4$ consumed for the blank titration of distilled water required for dilution of sample;

F = calculation factor for conversion of volume of the $KMnO_4$ solution used in titration into exactly 0.01 N standard solution; and

V = volume (in ml) of analyzed sample.

DETERMINATION OF ALUMINUM ANALYSIS

The aluminum content was determined spectrophotometrically using the solubility of the aluminum complex with 8-hydroxichinoline in chloroform. To 50 ml of filtered wastewater were added 10 ml of CH_3Cl, 10 ml of 5 percent solution of 8-hydroxichinoline, and 10 ml of 10 percent ammonium acetate. The sample was precipitated for several minutes. Next it was left for separation of the layers. The chloroform layer was separated. Extraction was carried out another two times using 10 ml of chloroform each time. The chloroform extract was collected and the extinction determined. The aluminum concentrations were read off from the standard curve.

When iron in the wastewater was an obstacle to determination, the sample was acidified and oxidized, and ammonium was added. The arising iron compound was extracted several times with isoamyl alcohol. After the iron ions in the sample had been removed, the aluminum was determined according to the method described previously. The method of determining aluminum was checked by using weight determination with the same reagent (8-hydroxichinoline).

APPENDIX B

METHOD OF DETERMINING FINAD INDEX

DETERMINATION OF PHENOL NUMBER

Principle of Determination

In an alkaline medium (pH about 10.0) and in the presence of potassium ferrocyanide, phenol with p-aminoantipyrine forms an indophenol dye, soluble in chloroform, colored greenish-yellow to orange.

Procedure

Increasing doses of carbon are added to 0.1 mg/l of phenol solution, amounting to from 2 to 50 mg/l.

After 3 h of contact time, 5 ml of the buffer solution (20 percent NH_4Cl in a 25 percent ammonium hydroxide solution) and, after mixing, 3 ml of 8 percent potassium ferrocyanide are added to 500 ml of the filtrate.

After 3 min, 15 ml of chloroform are added and the sample is extracted. The extraction is repeated with a second dose of chloroform and the combined extracts are filled up with chloroform in the cylinder to the volume of 25 ml. The measurement is made using the spectrophotometer at 460 nm. The result is read from the standard curve previously prepared [1].

Calculation

A Freundlich isotherm is plotted on double log-log paper:

$$\log \frac{x}{m} = f \times \log C$$

where: x = the amount of adsorbed phenol (mg/l),

m = carbon amount (g), and

C = final phenol concentration (mg/l).

The phenol index is read from the diagram by extrapolating the straight line to its intersection with the parallel one to the axis of ordinates at the point log 0.01. The obtained value from $\frac{x}{m}$ corresponds to the diminution of the phenol solution concentration from 0.1 to 0.01 mg/l. Then:

$$m = \frac{x}{y} = \frac{0.1-0.01}{y} = \frac{0.09}{y} \quad .$$

The phenol index = $\frac{0.09}{y}$ g of carbon.

DETERMINATION OF IODINE NUMBER

Principle of Determination

The iodine amount not bound by the carbon is determined volumetrically by means of sodium thiosulphate.

Procedure

To 20 ml of 0.2 N iodine solution is added 0.2 g of carbon. Then the solution is mixed for 4 min and filtered through a soft paper filter. The volumetric determination of the residual iodine amount is performed using 0.1 N sodium thiosulfate solution. Simultaneously, a blank test (without carbon) is carried out. This makes it possible to determine the residual iodine amount in the solution after adsorption on the filter [2].

DETERMINATION OF INDOLE NUMBER

Principle of Determination

Indole, together with sodium nitrite and sulfuric acid, forms a red-colored nitrozoindole, extracted by means of isoamyl alcohol and determined spectrophotometrically at 500 nm.

Procedure

An increasing carbon dosage from 2 to 20 mg/l is added to 1 l of the indole solution at the concentration 0.6 mg/l. After 30 min of mixing the sample 0.5 ml of 1 percent $NaNO_2$ and 2 ml of concentrated H_2SO_4 are added to 100 ml of the filtrate. After 2 h the arising color is extracted with 25 ml of isoamyl alcohol, and the sample is determined at 500 nm. The obtained result is read from the standard curve previously prepared [3].

Calculation

The Freundlich isotherm is plotted, and from the diagram the value y is read from $\frac{x}{m}$, corresponding to C = 0.1 where x = 0.5 and m = the indole index, and the indole index = $\frac{0.5}{y}$ g of carbon.

DETERMINATION OF PHENAZONE NUMBER

Principle of Determination

Antipyrine (phenazone) treated with iodine forms iodoantipyrine, soluble in chloroform. The nonbonded iodine amount is determined by means of sodium thiosulfate.

Procedure

Approximately 0.3 g of carbon is added to 50 ml of 0.4 percent phenazone solution and then mixed for 20 min. Afterwards, the solution is filtered through a hard filter, with the first 15 ml of the filtrate rejected.

To 25 ml of the filtrate are added 2 g of sodium acetate and 30 ml of 0.1 N iodine solution. The whole sample is then left for 20 min; then the precipitate is dissolved in 100 ml of chloroform, and volumetric determination by means of 0.1 N sodium thiosulfate ($NA_2S_2O_3$) is made. The blank sample (without carbon) was dealt with in the same way [2, 4].

Calculation

$$\text{The phenazone index} = \frac{0.94\ (N-n)}{p}$$

where: p = carbon amount in g,

N = amount of 0.1 N sodium thiosulphate ($NA_2S_2O_3$) solution in ml necessary for the volumetric determination of the tested sample, and

n = amount of the 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution necessary for the volumetric determination of the blank sample.

DETERMINATION OF DETERGENT NUMBER

Principle of Determination

Anionic detergents, including LSS, form with methylene blue a complex organic compound of a blue color, soluble in chloroform. The color intensity is measured spectrophotometrically at 652 nm and compared with the standard curve.

Procedure

Carbon doses increasing from 5 to 50 mg/l are added to 1 l of the LSS solution of a concentration of 0.25 mg/l. After 60 min of continuous contact, the LSS amount in the filtrate is determined. The 100-ml sample is alkalized in the presence of phenophtalein by means of 1 N of NaOH solution and afterwards acidified with sulfuric acid. Then it is transferred to a separator, and 10 ml of chloroform and 25 ml of methylene blue are added. (Thirty ml of 0.1 percent solution are added to 500 ml of water; then 6.8 ml of the concentrated sulfuric acid (H_2SO_4) and 50 g of $NaH_2PO_4 \cdot H_2O$ are added. After it completely dissolves, the sample is filled with distilled water to 1 l.)

The whole sample is extracted vigorously for 30 s and left for separation. The chloroform layer is transferred to another separator, and the extraction procedure is repeated twice more using 10 ml of chloroform.

In the second separator, 50 ml of rinsing solution is added to the combined extracts (6.8 ml of the concentrated sulfuric acid and 50 g of $NaH_2PO_4 \cdot H_2O$ are added to 500 ml of distilled water, and after the sample has been dissolved, it is filled up to the volume 1 l) and vigorously shaken. After settling, the chloroform layer is poured out into a 50-ml flask. The rinsing is repeated twice with the addition of 10 ml of chloroform. The chloroform extracts combined are filled to 50 ml with chloroform. The adsorption is determined at 652 nm [5].

Calculation

The Freundlich isotherm, $\log \frac{x}{m} = \log C$, is plotted and determined from the diagram, the value from $\frac{x}{m}$ corresponding to $C = 0.025$, where $x = 0.225$ and m = detergent index. The detergent index $= \frac{0.225}{y}$ g of carbon.

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Table B-1

Relationship between particular numbers and grades corresponding to them

Grade	0	1	2	3	4	5	6	7	8	9
		carbon	carbon	carbon	carbon	carbon	carbon	carbon	carbon	carbon
Solution		g	g	g	g	g	g	g	g	g
Phenol		0.0907	0.0803	0.0699	0.0595	0.0491	0.0387	0.0283	0.0179	0.0075
Iodine		52	62	72	82	92	102	112	122	132
Indole		0.013	0.012	0.011	0.010	0.009	0.008	0.007	0.006	0.005
Phenazone		6	9.4	12.8	16.2	19.6	23	26.4	29.8	32.2
Detergent		0.090	0.080	0.070	0.060	0.050	0.040	0.030	0.020	0.010

The FINAD value is obtained by comparing the grades read off from table B-1 in the following sequence: F (phenol), I (iodine), N (indole), A (phenazone), and D (detergents).

APPENDIX C

DECREE OF THE MINISTRY COUNCIL (extract)

dated: November 29, 1975
On the water classification and conditions which should be
fulfilled by wastewaters discharged to receiving waters.

In Poland three classes of purity have been laid down for inland surface waters:

1. The first class includes those waters which are intended for:

   a. drinking water supply,
   b. supply to an industrial plant requiring water of drinking water quality,
   c. breeding of fish of the salmon type.

2. The second class includes waters which are intended for:

   a. breeding of fish, with the exception of the salmon type,
   b. water supply for domestic livestock,
   c. organized bathing facilities,
   d. recreational purposes and water sports.

3. The third class includes waters intended for:

   a. supply to an industrial plant, except for those industries requiring water of drinking water quality,
   b. irrigation of agricultural land and greenhouses.

2. Table 1 of the decree defines the size of admissible pollutants of inland surface waters in individual classes of purity.

3. a. The pollutants contained in an average hour-long outflow of wastewater fed into inland surface waters cannot:

   1. cause an excess of admissible pollutants in the receiver in relation to the normal water flow in the place where the wastewater is fed in or in relation to the active volume of standing water,
   2. contain solid waste or settlable suspended solids which have been left for 2 hours in an amount greater than 0.5 cm^3/dm^3, or dangerous substances (DDT and PCB).

b. If the maximum hour-long outflow of wastewater exceeds by at least twofold the average hour-long of wastewater, the maximum outflow is taken as the basis for determining the conditions which the wastewater should fulfill.

c. The long term low-average flow of the receiving stream at the point of discharge has been adopted as the design flow to use in determining permissible waste loading.

Table C-1

Permissible pollutant concentration for surface waters

Parameters	Units	Purity class		
		I	II	III
1	2	3	4	5
Oxygen dissolved	mg O_2/dm^3	≥ 6	≥ 5	≥ 4
BOD_5	mg O_2/dm^3	≤ 4	≤ 8	≤ 12
Permanganate COD	mg O_2/dm^3	≤ 10	≤ 20	≤ 30
COD	mg O_2/dm^3	≤ 40	≤ 60	≤ 100
Saprobity		oligo to-betamezo	betamezo to-alpha-mezo	alpha-mezo
Chloride	mg Cl/dm^3	≤ 250	≤ 300	≤ 400
Sulfate	mg SO_4/dm^3	≤ 150	≤ 200	≤ 250
Hardness	meg/dm^3	≤ 7	≤ 11	≤ 14
Residue total filterable	mg/dm^3	≤ 500	≤ 1000	≤ 1200
Residue total nonfilterable	mg/dm^3	≤ 20	≤ 30	≤ 50
Temperature	°C	≤ 22	≤ 26	≤ 26
Odor		≤ 3R	natural	specific
Color	mg Pt/dm^3	natural		
pH value	pH	6.5-8.0	6.5-9.0	6.0-9.0
Nitrogen (ammonia)	mg N_{NH_4}/dm^3	≤ 1.0	≤ 3.0	≤ 6.0
Nitrogen (nitrate)	mg N_{NO_3}/dm^3	≤ 1.5	≤ 7.0	≤ 15.0

Table C-1 (con.)

Permissible pollutant concentration for surface waters

Parameters	Units	Purity class		
		I	II	III
1	2	3	4	5
Nitrogen (organic)	mg N_{org}/dm^3	≤1.0	≤2.0	≤10.0
Total iron	mg Fe/dm^3	≤1.0	≤1.5	≤ 2.0
Manganese	mg Mn/dm^3	≤0.1	≤0.3	≤ 0.8
Phosphate	mg PO_4/dm^3	≤0.2	≤0.5	≤ 1.0
Rhodanate	mg CNS/dm^3	≤0.02	≤0.5	≤ 1.0
Cyanides (without complex cyanide)	mg CN/dm^3	≤0.01	≤0.02	≤0.05
Complex cyanides	mg Me/CN(x) $/dm^3$	≤1.0	≤2.0	≤ 3.0
Volatile phenols	mg/dm^3	≤0.005	≤0.02	≤0.05
Detergents	mg/dm^3	≤1.0	≤2.0	≤ 3.0
Oils	mg/dm^3	-	-	-
Etheric extract	mg/dm^3	≤5.0	≤15.0	≤40.0
Lead	mg Pb/dm^3	≤0.1	≤0.1	≤ 0.1
Mercury	mg Hg/dm^3	≤0.001	≤0.005	≤0.01
Copper	mg Cu/dm<	≤0.01	≤0.1	≤ 0.2
Zinc	mg Zn/dm^3	≤0.01	≤0.1	≤ 0.2
Cadmium	mg Cd/dm^3	≤0.005	≤0.003	≤ 0.1
Chromium +3	mg Cr/dm^3	≤0.5	≤0.5	≤0.5
Chromium +6	mg Cr/dm^3	<0.05	≤0.1	≤0.1

Table C-1 (con.)

Permissible pollutant concentration for surface waters

Parameters	Units	Purity class		
		I	II	III
1	2	3	4	5
Nickel	mg Ni/dm^3	$\leq$1.0	$\leq$1.0	$\leq$1.0
Sum of heavy metals	mg/dm^3	$\leq$5.0	$\leq$15.0	$\leq$40.0
Silver	mg Ag/dm^3	$\leq$0.01	$\leq$0.01	$\leq$0.01
Vanadium	mg V/dm^3	$\leq$1.0	$\leq$1.0	$\leq$1.0
Boron	mg B/dm^3	$\leq$1.0	$\leq$1.0	$\leq$1.0
Arsenic	mg As/dm^3	$\leq$0.05	0.05	0.2
Chlorine, total residual	mg Cl$_2$/dm^3	-	-	-
Fluorine	mg F/dm^3	$\leq$1.5	$\leq$1.5	$\leq$2.0
Sulfide	mg S/dm^3	-	-	0.1
Acrilonitrile	mg/dm^{3}3	$\leq$2.0	$\leq$2.0	$\leq$2.0
Caprolactam	mg/dm^3	$\leq$1.0	$\leq$1.0	$\leq$1.0
Coli index		$\geq$1.0	$\geq$0.1	$\geq$0.01
Panthogenic bacteria		undetectable	undetectable	undetectable
Fish bioassay	24 h	positive-water should not cause death of fish in the course of 24 h		

GLOSSARY

abrasion number of activated carbon: Coefficient expressed in percentages, characterizing decrease in carbon grains above D=1 mm as a result of energetic shaking on sieves.

activated carbon moistness: Moisture content, expressed in percentages in relation to moist carbon.

adsorption isotherm: Quantity of adsorbed substance per unit of adsorbent related to the concentration of adsorbate at equilibrium.

adsorption rate: Amount of pollutant removed in milligrams per gram of carbon and per hour.

ash content: Amount of ash, in percentages, remaining after the carbon has been scorched at 850° C in relation to carbon weight.

bed porosity: Relation of volume of all free spaces to total carbon volume.

bulk density of carbon: Weight of 1 l of activated carbon poured and crushed, in terms of dry carbon.

carrier: Chromatographic column filling and chromatographic plate covering.

chromatogram: In column chromatography--the sorbent column after expansion and development of separated substances; in thin-layer chromatography--the plate covered with a sorbent layer with clear stains of separated substances.

coagulant: A chemical agent added to wastewater in order to carry out coagulation.

coagulation: A physicochemical process consisting of the removal of pollutants from wastewater by means of flocculation and sedimentation of suspended solids, precipitation of compounds that are difficult to dissolve, and adsorption on a solid phase.

color according to the Pt scale: Wastewater color compared with standards of the platinum-cobalt scale.

color threshold: Dilution expressed by the number of milliliters of wastewater in 100 ml of water necessary for the color of this mixture to be close to natural color.

column chromatography: Analytical technique consisting of the separation of components of a mixture on chromatographic column filling.

condensation of samples: Removal of water through evaporation under normal pressure or in a vacuum.

contact coagulation: Method of coagulation whereby a coagulant salt is added to the wastewater influent to the upflow gravel-sand filtration bed; coagulation occurs in the filtration bed.

content of substances dissolved in hydrochloric acid: Mass of dry residue, in percentages, obtained after the carbon has been boiled in hydrochloric acid in relation to carbon weight.

content of substances soluble in water: Mass of dry residue, in percentages, obtained after the carbon has been boiled in 200 ml of distilled water, in relation to carbon weight.

conventional coagulation in a reactor with suspended flocs: A method of coagulation whereby wastewater with coagulant added flows through a layer of suspended flocs, in which the coagulation process occurs.

developing the chromatogram: Filtration through the column with a band of pure solvent previously adsorbed on it or with an admixture of strongly surface-active substance.

dye capacity of resins: Amount in milligrams of dye absorbed on 1 ml of resin in defined reaction conditions.

dynamic activity: Adsorptive capacity expressed by time lapse of protective activity of the activated carbon layer from the moment adsorption begins up to the moment traces of vapors and gases appear behind the carbon layer.

eluation: Gradual dissolution of separated substances in a column or on a thin-layer plate with water or other suitably chosen solvents.

eluent: In thin-layer and column chromatography, the fluid used to wash out the substance from the column or from the thin-layer plate.

exchange capacity for wastewater: Alkalinity of wastewater expressed in milligrams of $CACO_3$ in relation to 1 l.

exchange capacity of resin: Maximum number of ions, in milligram-equivalents, which can be linked by 1 ml of resin.

extraction: Individual operation used to separate fluid or solid mixtures; the component from the extracted phase is transformed into a solvent.

FINAD: Index defining adsorptive properties with regard to five pollutant parameters: phenol, iodine, indole, phenazone, and detergents.

granulation: Measurements of grains (particles) of carbon, given in millimeters.

GLOSSARY (continued)

hydraulic loading BV/h: Bed loading per hour.

macropores: Pores with radii of about 10,000 Å.

mechanical endurance: Fraction of activated carbon, in percentages, not subject to disintegration in a ball mill.

methylene number: Number of milliliters of 0.15 percent methylene blue decolorized by 0.2 grams of activated carbon.

micropores: Pores with radii of about 10 Å.

milligram number: Number of milligrams of activated carbon necessary for decolorizing 200 ml of standard solution of molasses.

ozone dose mg/l: Amount of ozone fed into 1 l of wastewater.

porometric determination of pore size: Method of determining capillary volume at radii less than 100 Å.

porosity of activated carbon: Carbon property of having pores, i.e., open or closed spaces and channels of different diameters.

porozimetric determination of pore size: Method of determining capillary volume at radii in the range of 75,000 to 100 Å.

regeneration capacity: Relation, in percentages, of the amount of activated carbon obtained as a result of regeneration to the amount of carbon before regeneration.

regeneration of ion-exchange resins: Transforming the exhausted ion-exchange resin again into a chloride or hydrogen form.

subgrain: The grain which remains after sifting, although the dimension of this grain is smaller than that of the sieve openings.

thermal regeneration: Regeneration consisting of the burning of pollutants at a temperature of about 800° C in the presence of or without steam.

tar and oil substance content in carbon: A test consisting in boiling down activated carbon in 10 percent solution of sodium hydroxide and ascertaining whether the filtrate is colorless.

thin-layer chromatography: Analytical technique consisting in the separation of components of a mixture on a chromatographic plate; the migrational center of separated substances is constituted by a suitably prepared plate covered with a thin layer of sorbent.

total capacity of resins: Number of milligram-equivalents (meq) of ions removed by a volume of resin (ml).

total surface area activated carbon: Total surface area corresponding to a unit of activated carbon mass, measured by the BET method.

volatile substance content in carbon: Number of volatile parts in the carbon, expressed in percentages, in relation to carbon weight.

water absorptivity: Pore volume accessible for water expressed in grams of water per 1 g of carbon.

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